

psa

JOURNAL

SECTION **b**

PHOTOGRAPHIC SCIENCE AND TECHNIQUE

A quarterly technical supplement to PSA Journal

SUBMARINE PERISCOPE PHOTOGRAPHY

BY J. C. MILLIGAN

A brief description is given of the space in which a photographer must work when he is using the periscope as a camera. The problems of record and reconnaissance photography are discussed and the available externally mounted cameras are described. Exposure determination, focusing procedures, the use of ray filters, and the processing and printing of film aboard a submarine are discussed.

THE COVER PICTURE shows an MK 4 still camera in operation on a submarine periscope as might be required on a photographic reconnaissance mission.

Published with Vol. 19, No. 2



TABLE OF CONTENTS

THE PRESENT STATUS OF DIRECT NEGATIVE-POSITIVE COLOR PRINT PROCESSES IN EUROPE. II. POSITIVE PRINT MATERIALS AND PROCESSING	H. GORDON	5
TWO-BATH FIXATION OF PRINTS	J. I. CRABTREE, R. W. HENN, AND R. F. EDGERTON	10
PHOTOGRAPHIC STANDARDS FOR CAMERA SHUTTERS	VERNON E. WHITMAN	17
SUBMARINE PERISCOPE PHOTOGRAPHY	J. C. MILLIGAN	19
ON THE MECHANISM OF PHOTOGRAPHIC SENSITIVITY IN SILVER BROMIDE	CONTRIBUTED	22
MODIFICATION OF LACQUERS FOR PROTECTIVE COATING OF PHOTOGRAPHS	HUBERT O. RANGER	23
MOTION PICTURE AND FLASH PHOTOGRAPHY IN MECHANICS RESEARCH	CLIFFORD C. HAUVER	27
HIGH-SPEED PHOTOGRAPHY IN MEDICINE	JOHN H. WADDELL	29
SOME DESIGN FEATURES OF A WIDE-FILM CONTINUOUS PROCESSING MACHINE	J. S. GOLDHAMMER	32
INFLUENCE OF QUATERNARY SALTS ON PHOTOGRAPHIC DEVELOPMENT AND THEIR EFFECTIVENESS AS CHROMATOGRAPHIC DEVELOPERS	W. VANSELOW AND T. H. JAMES	36
BOOK REVIEW	IRA B. CURRENT	40

FIRST 1953 ISSUE ☆ VOLUME 19B, NUMBER ONE ☆ PUBLISHED WITH THE PSA JOURNAL FOR FEBRUARY 1953

PHOTOGRAPHIC SCIENCE & TECHNIQUE

EDITOR, PAUL ARNOLD, APSA
26 Hotchkiss Street, South
Binghamton, N. Y.

ASST. EDITOR, H. LOU GIBSON, FPSA
343 State Street
Rochester 4, New York

LAWRENCE B. FRIAR
R. C. HAKANSON
HUTSON HOWELL
PETER KRAUSE, APSA
HERBERT MEYER
JOHN B. TAYLOR

DIVISION AND ASSOCIATE EDITORS

P.O. Box 1009
10322 Lake Shore Boulevard
700 Commonwealth Avenue
69 Bourndale Road, South
1421 Northwestern Avenue
118 Laurel Avenue

Rochester 3, New York
Cleveland 8, Ohio
Boston, Massachusetts
Manhasset, New York
Hollywood 27, California
Binghamton, New York

PHOTOGRAPHIC SCIENCE AND TECHNIQUE is prepared four times yearly for the Photographic Society of America by its Technical Division. It is published as SECTION B of PSA Journal but the issues are separately numbered and page numbered. It is mailed without additional charge to all Society members and to Journal subscribers. Separate subscriptions are not available.
Individual and camera club membership in the Society, in-

cluding subscriptions to both publications, may be obtained from PSA Headquarters, 2005 Walnut Street, Philadelphia 3, Pennsylvania upon payment of \$10.00 annual dues. Institutional and library subscriptions to both publications are available at \$5.00 a year. No extra charge is made for mailing to foreign countries.
Address all manuscripts and communications to the Editor. Unacceptable manuscripts will be returned promptly. The

contents are copyrighted in the U.S.A. but permission to reprint will be given for any reasonable request.
The PSA Journal is printed in the U.S.A., published at Orange, Connecticut and entered as second class mail at the Orange, Connecticut Post Office. The publishing of opinions expressed by authors does not necessarily indicate concurrence or endorsement by the editors, by the Technical Division or by the Photographic Society of America.

THE PRESENT STATUS OF DIRECT NEGATIVE-POSITIVE COLOR PRINT PROCESSES IN EUROPE

II. POSITIVE PRINT MATERIALS AND PROCESSING

H. Gordon*

FOREWORD

The first part of this paper deals with the color negative materials being marketed at present in Europe. Agfacolor from the Agfa plant in the Western Zone at Leverkusen, Germany; Gevacolor from Gevaert in Morstel, Belgium; Ferranacolor from Turin, Italy; and Telcolor from Tellco in Fribourg, Switzerland were described in detail. Brief reference was also made to prewar Agfacolor negative film from the Wolfen, Germany plant and to present production from the same source under Russian administration. This second part deals with the positive color paper printing materials provided by the same four European manufacturers for printing their respective color negatives.

THE RESULTS obtainable with the four European color negative film types reveal a close similarity in their general character if mask development has not been carried out. Each product, regardless of the manufacturer, has its characteristic color tint, but it is not always possible to differentiate the various makes by a specific color tint if they are examined after development. However, the spectral transmission of the formed dyes is very different in the individual makes so that unfiltered test prints immediately show a strong shift when two identically appearing negatives of different manufacture are printed. Nevertheless the various film types can be printed on color papers of different origin provided that suitable printing filters have been selected.

The following characteristics may be mentioned to differentiate between the developed film types. Agfacolor Negative films size 120 from Leverkusen carry markings at the end of the film designating them as "Agfacolor T" or "Agfacolor K" depending on whether daylight (*Tageslicht*) or artificial light (*Kunstlicht*) film is in question. In addition the current emulsion number is printed on, which permits identification of daylight and artificial light film, as well as the date of manufacture. The knowledge of these figures is important for the printing process. The Agfacolor Negative film from Wolfen (or Photoplenka) does not have such an identification, nor do the size 120 films of the other three makes. Density and color of the background fog vary widely. The Wolfen Agfa films of this type use heavier film base than the other makes. The mask-developed film types are readily recognizable by their gray fog.

The 35mm films of Agfa (Leverkusen) carry the name of the firm printed along the edge outside the perforations as well as serial numbers, for the frames, from 1 to 20 or 1 to 40 respectively. Those films with the designations B (*Bogenlicht*) and G (*Glühlicht*) in place of T and K (B for arc light; G for incandescent light) are out-of-date.

Gevacolor film in 35mm width bears the firm's name at the perforation edge, otherwise only the number of the running foot length appears, because it is available only as cine film.

The dyes which can be obtained by processing a paper whose layer structure is the same as that of the negative materials are produced by chromogenic development in the paper emulsion. In the chemical aspects there is full analogy in principle to the

negative process. However, there are technical differences, depending on the special paper type.

It is necessary that the sensitization of the paper types be adjusted for the transparency curves of the dyes present in the negatives. The sensitization of the film is chosen so that the curves of the dyes in the negative overlap, whereas those of the print are separated sharply from each other.

Light Balancing Filters

The filter sets of the different manufacturers for color balancing the printing light have this in common: there are eleven filters of different intensity for each of the three primary colors yellow, magenta, and cyan. The step subdivision is the following:

05
10
20
30
40
50
60
70
80
90
100

The sum of the three filters that are designated by the number 100 should be equivalent to the density 1.0. There are in all 33 filters which can be used in the printing process. Two questions arise: Which filter strength is necessary to compensate for a color tint present in a filterless test print? And, how great is the consequently necessary increase of the exposure time for the print? The filter chosen must have the color that, from observation of the test print, needs to be *diminished*. This is a necessary detail of a color negative-positive printing process that is the direct opposite of the practice with a direct reversal material such as Printon.

Selection of the proper intensity of the correction filters is a matter of experience. The filter set to be chosen may be one of the three primary colors or it may be a combination of two perhaps very different intensity filters of the primary colors. In filter calculations one may possibly have to subtract the lowest intensity. These conditions should be emphasized because photographers having experience only with Printon are not familiar with them.

Examples of the exposure increase for filters of different density are given by Agfa (Leverkusen) in tables published

* Swedish Colorphoto Corporation, Stockholm 1, Sweden. Received 9 July 1952. Translated from the original German by G. A. Wieschahn. Part I appeared in the October 1952 issue.

Table III
CORRECTION OF PREDOMINANT COLOR TINT

Negative-Positive Method		Transparency-Reversal Positive Method (Printon)	
Predominant Color of Test Print	Correction Filter Required	Predominant Color of Test Print	Correction Filter Required
yellow	yellow	yellow	cyan + magenta
orange	yellow + magenta	orange	cyan
red	magenta + yellow	red	cyan + yellow
magenta	magenta	magenta	yellow + cyan
violet	magenta + cyan	violet	yellow
blue	cyan + magenta	blue	yellow + magenta
cyan	cyan	cyan	yellow + magenta
green	cyan + yellow	green	magenta

for use with their products. If a filterless test print is made and the exposure chosen by experience was correct, the increase in time for the use of the necessary filter combination may be found in the Agfa table. The time increase is critical, and therefore exact timing with an exposure clock is necessary.

The table of filter factors is valid only for the Agfa filter set. For the filter sets of the other manufacturers the increase factors vary from case to case. Although the sets of the different makers are based upon the same principle, neither the dyes used for the three primary colors are identical, nor are the dye concentrations alike. An exchange of the filter sets in the use of a certain paper type therefore has limitations.

The prevailing conditions with respect to density and color shade deviations are presented in Table Four by comparing the filters of Agfa, Gevaert, and Ferrania with each other.

In Figure 1 the transmission curves for the dyes used in the Gevaert filter set are reproduced for the concentration designations 50 and 100. The dyes used seem to correspond in most cases to Filter Yellow, Acid Fuchsin, and Patent Blue. The difference in the dyes used by the different manufacturers re-

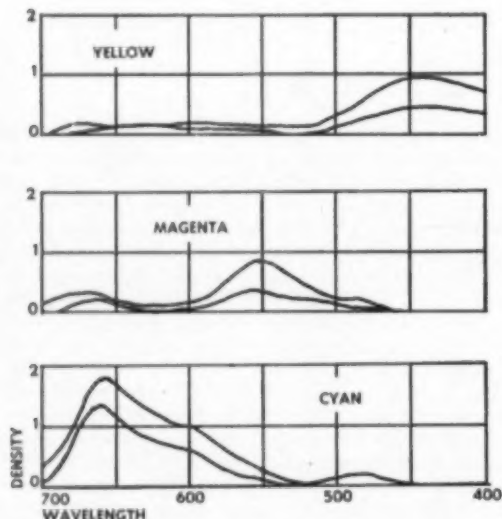


Fig. 1. Spectral transmission of Gevacolor printing filters. The intensity of the filters is 50 and 100 units respectively. Data obtained from measurements with a Zeiss-Goldberg Spectrodensograph.

sults from the most favorable transparency conditions for the optical sensitization in the different layers of the material in question.

A certain effect on the color reproduction naturally results from the color of the glasses between which the filters are mounted. If the glass is colorless, there is no disturbance of the color balance. If the glass shows a typical blue-green inherent color, filter corrections are necessary. Tests with colorless and blue-colored condenser lenses in the enlarger readily demonstrated the great importance of this difference in the color of glass so that, in a color printing laboratory, different enlargers of the same type show correction factors if they are not equipped with condensers of the same type. The inherent color of the objective lenses has the same effect.

Mosaic Filters

A special class of filters are the so-called mosaic filters. The purpose of these arrangements is the determination of the most favorable filter combination. This is valid especially if one has to work with an unknown color negative emulsion, an unknown color paper, or with both simultaneously. The determination of the optimal filters by mosaic filters is based on the following: The basic filters

yellow + magenta
yellow + cyan
magenta + cyan

are combined with each other in their most important densities so that all possible densities are represented in each of these three filters in their combinations. Consequently there are 25 filter combinations in each mosaic filter on the basis of distances of 20 filter units. An interpolation is then possible off hand. These mosaic filters are very well suited for carrying out orientation experiments if one has no knowledge whatsoever about the color tint of a certain combination.

It is advisable to proceed by first trying to determine with the aid of a filterless test print (1) the exposure time, (2) the predominant color tint. Whereas the exposure time can readily be determined by a few tests, the color tint of the test print is not always unambiguous. If the print shows it distinctly, the corresponding filter combination in the color of the tint is chosen. For example, if it is brown, we have a combination of yellow and magenta, and with the aid of the mosaic filter we can determine the most favorable fractions of yellow and magenta densities respectively. It is advisable in exploratory tests with this mosaic filter to employ twice the exposure time which has been found suitable for the zero print. It is also important—and this is not always easy—to place the mosaic filter on the most important area of the picture.

Additive Printing

It is also possible to print the color negative successively through the three separation filters (red, green, and blue). This, however, requires the previous factor determination of each of the filters. The making of separation positives for purposes of the motion picture technique can be carried out in the same manner.

Sensitivity Characteristics of Color Papers

In the following the different properties of the four printing papers for the negative process are briefly discussed. The overall speed is the same for all; it corresponds approximately to that of bromide paper of normal gradation. Far different from

Table IV

FILTER DENSITY AND COLOR SHADE (VISUAL)

Color Shade	Ferrania	Agfa	Gevaert
yellow	10 20 15	50 80 60	100 170 140
magenta	... 10 20 20 05	... 50 85 05 ... 70 05	... 100 170 10 ... 130 10
cyan	... 10 05 ... 20 10	... 50 05 ... 80 15 40	... 100 05 ... 150 ... 30 100

The sequence of the figures is always yellow-magenta-cyan.

normal bromide paper, but common for all four color papers, is the darkroom illumination specified for their processing. The papers have a sensitization gap so that indirect sodium light of reduced intensity is permissible. In other words, monochromatic light of 589 m μ can be used.

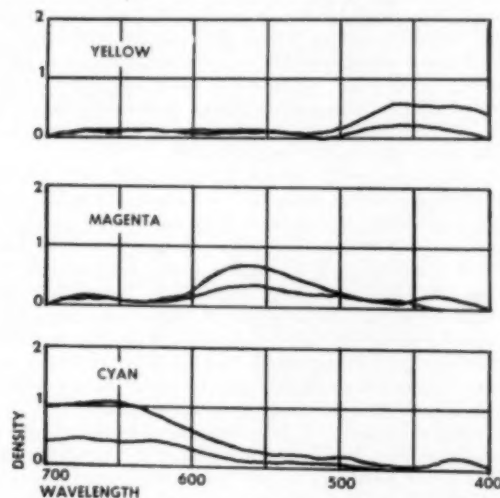


Fig. 2. Spectral transmission of Agfacolor printing filters, 50 and 100.

It is simpler to employ for direct illumination of the work benches customary darkroom lamps with filters having the same absorption but of broader slope. Especially suitable are the filter combinations of Gevaert. An orange-red bulb is combined with a light green filter so that only the harmless range in the neighborhood of 590 m μ is transmitted, resulting in an illumination which is very bright for the eye and makes possible all required operations. The darkroom filters for the other makes contain dye combinations with a similar transparency area, but for use in combination with weaker lamps.

Agfacolor Paper

Agfacolor paper is coated on material of cardboard thickness and contains the three emulsion layers in the classical sequence of the tripack; i.e. yellow, magenta, and cyan. Between yellow and magenta there is the orange-colored filter layer which is required to obtain the necessary color separations by suppressing the inherent blue-sensitivity of the silver bromide emulsions. During the processing this interlayer is decolorized. However, this bleaching is never quite complete so that a pure

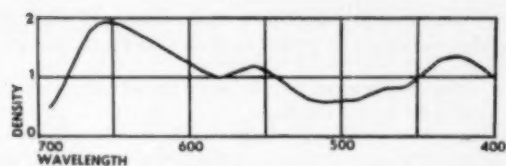


Fig. 3. Sum of Gevacolor 100 yellow, magenta, and cyan printing filters; spectral transmission. For the measurements used in the above, as well as Figures 1 and 2, the author is indebted to Professor Helmer Backstrom, Royal Institution of Technology, Photographic Department, Stockholm, who kindly permitted use of the apparatus.

white background can never be obtained on Agfacolor paper. It has been found that the colloidal silver can lead to side reactions with the bleach bath whose brownish products can no longer be removed from the layer system during the processing. This defect was avoided in other papers by changing the sensitization.

It is generally true for the Agfacolor paper as for all other papers to be described that the integral tripack here, as in the negative films, contains in each of the three layers sensitizing dye and color former as additions. It is obvious that neither the sensitizing dyes nor the color couplers can be fully the same as in the negative films because the required spectral reflection curves should correspond to a high degree to the subject colors.

Besides the sequence of the color forming layers may, under certain circumstances, be changed for practical reasons because of the required sensitization curves.

The paper is sold cut to all standard sizes, up to 50 × 60 cm, and because of the wide distribution of square negative sizes it is also obtainable in several square types. As in the negative emulsions, the tendency to dominant color tints varies widely from one paper emulsion to another. The manufacturer indicates on the package a basic filter number which is derived from a rather complex filter calculation system. It should permit the recalculation of the filtration of known negative types for the change from one paper batch to another emulsion number. For constant developing conditions the tints due to the emulsion can be considered as constant.

Gavacolor Paper Characteristics

The Gevacolor paper has an appearance different from the Agfacolor paper. As in the papers described later, the emulsion in the unexposed state superficially resembles a normal bromide emulsion. It has only a weak yellowish green coloration and not the typical brownish tint which the yellow filter layer confers on Agfacolor paper. By a suitable shift of the layer sensitization it has been possible to avoid the mentioned interlayer filter. This fact is of great value for the final result. It is much easier to obtain pure whites on Gevacolor paper because there can be no reaction between the colloidal silver filter and the bleach bath in the presence of traces of developing agent.

The layer structure of the older Gevacolor papers deviates from the normal sequence of the tripack emulsions. It is true that the yellow-forming layer also lies uppermost, but the magenta- and cyan-forming layers have been exchanged so that the magenta layer is the lowest. In the modern emulsions the classical layer sequence of the tripack has been restored. Simultaneously the color formers have been considerably changed so that brilliancy and light-fastness could be significantly improved.

Gevacolor paper is coated on a support some 30% heavier than the Agfa paper. This paper is also sold in numerous standard sizes.

For the Gevacolor paper too the manufacturer indicates basic filter numbers. It is pointed out at once that these are valid only for a certain standard enlarger of the manufacturer, and that therefore it is necessary to calibrate the apparatus in use in the processing laboratory relative to the indicated filters. A constant for the apparatus must be determined, which can only be an average value from a larger number of measurements.

In processing Gevacolor paper, at least the older emulsion numbers, it has been found that the determination of the exposure time is considerably more critical than for Agfacolor paper; the Schwarzschild exponent plays a significant role here. This is apparent in a tendency of underexposed prints to acquire a bluish tint, with the same filtration as for the normal exposure time, i.e. to show underdevelopment in the yellow-forming layer. With overexposure, on the other hand, the yellow-producing layer develops much more strongly because there is no proportionality any more. The enlarging scale is here—as with the other papers—of importance for the filter selection. It is therefore not possible to use the same filters for different sizes of the same negative. Variation in reciprocity law failure in the three layers is the cause.

Another characteristic of Gevacolor paper, pertaining only to the older emulsion types, may be pointed out. Because of the instability of the sensitizing dyes for the red-sensitive part, the manufacturer recommended storage of the material at a temperature of 2 to 3°C to prolong the shelf life. For the more recent emulsions this precaution is no longer necessary.

Ferraniacolor Paper

In appearance the Ferraniacolor paper resembles the paper of Agfa except for the fact that a colored interlayer is not required. It is therefore possible with this paper also to obtain pure whites without difficulty. The gradation is similar to that of Gevacolor paper, somewhat more brilliant than that of Agfacolor. This high gloss material of cardboard thickness is available in most standard sizes.

Telcolor Paper

Contrary to the types mentioned so far, Telcolor paper is sold only as thin (single weight) paper which makes its processing less convenient. Here too the emulsion has a color similar to that of an ordinary bromide emulsion, without filter interlayer. The arrangement of the layers is normal; i.e. as described for Agfacolor. The surface of the Telcolor paper is not of high brilliance but shows a fine graininess.

To simplify the filter determination, each paper package supplied by Tellko contains a test negative of standard motion picture size (18×24 mm) with a test print made at the factory. On its back the filters are mentioned which have been used for this print. This simplifies greatly and facilitates the control of the apparatus used and the processing technique of the purchaser's laboratory.

All European color papers have one characteristic in common. In all cases the appearance of the developed color picture changes greatly during the drying. The brilliance generally increases but the color tone too undergoes certain changes, mostly with the result of a more bluish tone. This change was especially pronounced in the older emulsions of the Gevacolor paper. The color of the yellow layer in the wet state fluoresces, covering the picture surface with a weak greenish "fog." How-

ever, this "fog" disappears completely during drying with an apparent approximately doubling of the maximal density of the picture. Newer types of Gevacolor paper with changed color components can be judged immediately after fixing because no substantial shifting of the color balance occurs afterwards.

Processing Color Papers

The processing technique for the color papers, like that for the negative films, has some common traits. The exposure technique as well as the developing technique and the after-treatment follow the same principles. The exposure can be carried out by contact printing or by enlarging and here the technique of the filter application as discussed above is of greatest significance. It is unessential whether one uses contact printers or enlargers. The use of the proper filters, the placement of the filters in the most favorable location, and the determination of the correct exposure times are always decisive for the quality of the resulting color reproduction.

As far as contact printers are concerned, they must be equipped with incandescent lamps of the proper color temperature. Gas discharge lamps of any kind are entirely unsuitable as light sources for this process. Only incandescent lamps emit a continuous light with homogeneous energy distribution throughout the visible region of the spectrum. It is for this characteristic that the filter sets have been adjusted.

The color temperature of the lamps should be 2,900 to 3,000K, the region for which the filter sets are applicable. However, care must be taken to keep the voltage constant. For this purpose automatic voltage regulators are available. Besides it is advisable, if one makes use of such devices, to maintain the working voltage about 10% lower than the normal lamp voltage and to adjust the filtration accordingly. This achieves the effect that the emission of the lamp remains constant for a much longer period of time.

In the contact printer the lamps—there may be one or several—are mostly mounted without condenser at a certain distance from the negative. It is recommended to equip the contact printer with a drawer which permits the insertion of the filters in closer proximity to the lamp than to the negative and facilities changing the filters. It must be possible to insert four filters of normal glass thickness at once. The distance from the negative should be fairly long to avoid the occurrence of any streaks or shadows on the print. It is not necessary to insert ultraviolet- or infrared-absorbing filters into the light beam, as is recommended, for example, for the Printon printing technique. Apparently the regions of the sensitization of the color papers are located so that no trouble is encountered either in the ultraviolet or the infrared.

For enlargers, generally the same rules hold true with regard to the regulation of the light color by printing filters. Common for all color printing enlargers is the necessity for the presence of a so-called filter drawer between light source and condenser which permits the insertion of four filters of the same set. It is also necessary to employ an opal lamp for enlarging purposes and to maintain the voltage constant. The "Omega D 2" enlargers have rendered good service. However, there are numerous other special enlargers, mostly of German and Italian origin, which are satisfactory. Some of them are even equipped with continuous filter control.

Exact measurement of the time is of greatest importance for making enlargements in the color print processes. It is necessary to reproduce the employed exposure times with certainty.

Exposure Determination

There are several means to determine the required exposure time. The method mostly used in practice starts with the test print whose exposure, after some experience with the printing material, can be judged rather accurately. Of course, it is possible to employ measurement with a Bunsen photometer or a similar instrument which takes into account the range of contrast of the negative, but such a method is much more time-consuming.

After the exposure time of the test print has been determined, a test print is made using the filter combination indicated on the basis of the observed color tint. In many cases the mosaic filter described above can help. If there is a possibility of taking a test image with color chart on the film roll to be used, it is a great aid for the determination of the basic filtration. This is especially true if the color chart contains a neutral gray wedge. The color tint is more readily recognizable on the reproduction of this gray wedge than by any other method.

To simplify the determination of the exposure time someone who works much with the same negative material can make a density collection of various standard negatives of the same emulsion for comparison purposes. A number of other methods have been recommended for the basic test, but we do not consider them here.

Table V

Steps	PAPER PROCESSING			
	Agfacolor	Gevacolor	Ferrania	Telcolor
development	3' 18"	4' 20"	3' 18"	3' 18"
rinse	10'	10'	5'	10'
stop	5'	5'		...
fixer			5'	
rinse	3'	30'	10'	...
bleach	3'	5'	1.5'	
rinse	3'	30'	1.5'	6'
fixing bath	3'	5'	5'	
rinse	...	5'
stabilizer	...	5'
rinse	20'	20'	15'	20'

* end of darkroom processing

Color Paper Processing Details

The treatment technique of all four paper types during processing is generally the same and essentially corresponds to the steps of the negative process. However, there are differences in the composition of the baths which are quite considerable. The steps are as follows:

	Negative Process	Positive Process
1.	development	development
2.	stop bath	stop bath
3.	bleach	bleach
4.	fixing bath	fixing bath

In this general table no attention has been paid to the required intermediate rinses or to baths which may be omitted eventually. The following comparison table presents the exact data on the specific conditions for each one of the four paper types.

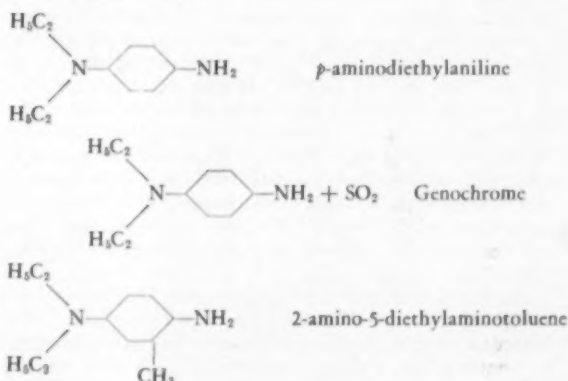
In order to gain an idea about the composition of the baths we reproduce here the processing directions for Agfacolor paper with all details. It may be that these data contain minor deviations from the unpublished directions employed at the present by the Agfa plant.

AGFACOLOR POSITIVE PROCESS:

1). Developer:	p-aminodiethylaniline hydrochloride	2.2 g
	hydroxylamine hydrochloride	2.0 g
	sodium sulfite	0.5 g
	potassium bromide	0.5 g
	potassium carbonate	75.0 g
	water, to make	1.0 liter
2). Stop Bath:	Sodium thiosulfate	300 g
	sodium sulfite	13 g
	potassium metabisulfite	12 g
	acetic acid (glacial)	15 ml
	potassium alum	15 g
	water, to make	1 liter
3). Bleach:	potassium ferricyanide	20 g
	monopotassium phosphate	12 g
	disodium phosphate	8 g
	water, to make	1 liter
4). Fixing Bath	sodium acetate	72.0 g
	sodium benzenesulfinate	2.4 g
	potassium alum	36.0 g
	sodium thiosulfate	80.0 g
	water, to make	1.0 liter

The composition of the color developer for the other three makes is closely related to the one for Agfacolor just described. The color developing agent may be the same in all cases, although perhaps one or the other manufacturer may use another derivative of the mother compound. As mentioned already under the negative process, Gevaert has recommended besides the possibility of the use of the *p*-aminodiethylaniline hydrochloride special agents designated as Gevaminol and Gevadiamin C. Ferrania employs a code number only, and Telco has furnished no data, but analysis revealed the presence of the mentioned amine as well as that of hydroxylamine. These color developers, after dissolution, must be stabilized by standing for at least 12 hours, because during the first hours after their preparation very annoying deviations of the color reproduction are encountered. No explanation has been found for this phenomenon.

It is known that there are a number of other color developing agents of related structure which can be used for the development of the color papers. We mention Genochrome, a sulfite compound of the *p*-aminodiethylaniline, and the 2-amino-5-diethylaminotoluene monohydrochloride. Both compounds can be used in appropriate quantities for the mentioned developer, but they cause considerable shifts in color and thus require filter changes.



With all brands long rinses after the development are called for although the duration varies from one case to another. Gevacolor makes an exception with regard to the length of the

washing; the rinse prior to the stop bath amounts to 10 seconds only. For Ferrania the time is 5 minutes, for Telco 10 minutes. There are therefore considerable differences of opinion as to the advantage of an after-development during the washing process.

The combined stop and fixing bath can be used in the same composition for Agfacolor and Gevacolor paper. Ferrania is satisfied with a neutral fixing bath. Telco finally dispenses with a stop bath completely; its paper processing employs two baths only. The duration of the stop bath in all cases is 5 minutes. Wide differences exist, however, in the duration of the washing after this stop bath. For Agfa paper 3 minutes suffice; for Gevacolor 30 minutes are required, and Ferrania is satisfied with 10 minutes.

The duration of the bleach bath for Agfacolor amounts to 3 minutes, whereas for Gevaert 5 minutes are required. Differences in the pH value and presumably of the layer thickness furnish the explanation; otherwise the two baths are very similar in composition. A much shorter time in the bleach bath is required by Ferrania, and for this material the composition of the bleach bath is very different from the two others. It is therefore reproduced here:

Copper sulfate	30 g
ammonium chloride	20 g
potassium bromide	25 g
water, to make	1 liter

The bleach bath which Telco employs at this step has not been published. However, it seems that ferric salt complexes together with sodium thiosulfate are the essential components. A combined bleach-fixing bath of somewhat lower keeping quality can be obtained as 5% solution of potassium ferricyanide and ammonium thiocyanate.

The rinses after the bleach bath are of very different lengths:

Agfacolor	3.0 min.
Gevacolor	30.0 "
Ferraniacolor	1.5 "
Telcolor	15.0 " as final wash.

The final fixer is for Agfa and Ferrania a hardening fixing bath of low sodium sulfite content.

For all brands except Gevaert there follows the final wash; but for this product another intermediate rinse of 5 minutes is prescribed to be followed by a stabilizing bath of the same duration. This is necessary to inhibit the slow self-decay of the yellow layer dye. Only afterwards follows the final rinse.

Summarizing we can say that with regard to the working time in processing it is by far the simplest and shortest for Telco. For Agfa and Ferrania the sum total does not differ much, but for Gevacolor the conditions in this respect with over 2 hours are rather unfavorable. It is obvious that intensive work is being done with the last-mentioned process to shorten the treating time, but experiments have proven that an abbreviation of the washing times always is accompanied by a degradation of the results. The two other processes, Agfa and Ferrania, also endeavor to shorten and to simplify the processing in the direction of the Telcolor development.

The image character can be influenced considerably by a change of the developing time for the paper prints. With Agfacolor paper the standard developing time of 3 minutes can be lengthened to 6 minutes if a higher contrast is desired. This, however, requires a change of filters; for there is a shift towards magenta. Besides there is a tendency to stain the whites. With Gevacolor, which is especially well liked here in Sweden, it has been possible to maintain the whites very pure

during standard development. The change of the picture tone with variation of the developing time results in a shift towards cyan with shorter development and a shift towards yellow if development is prolonged. The same holds true for changes in the temperature between 18 and 22°C. The gradation with shortened development becomes softer.

To carry out the described developing process there are two possibilities which depend on the number of prints to be made simultaneously as well as on the material used. The simplest case is that of tray development which can be carried out with all described processes. Here only one important point must be watched, and that is the maintenance of the prescribed temperature of the developer. It is necessary that the temperature (18 or 20°C respectively for the different processes) is kept constant for the time of the development because otherwise uncontrollable deviations in the color rendition occur. In this case a developing tray in a water bath with thermostatic equipment is advisable. The prints must be kept constantly in motion in the baths in the same manner which is customary in black-and-white development so that they do not stick to each other. The prescribed washings must be very thorough. Here, too, sticking together must be avoided by suitable circulation.

Whenever the simultaneous treatment of a larger number of prints is to be carried out, for example, in an industrial laboratory, the processing is best accomplished in a series of tanks. A practical apparatus consists of 15-liter tubes of a plastic material, the number of which depends on the formulae to be employed. Some of them are filled with the baths, while the others are equipped with circulating wash water. The prints are placed in baskets, also of a plastic material, in a half-rolled condition. The baskets are standardized for different sizes, and each print is in a separate pocket. These baskets, which contain numerous perforation holes to permit easy access for the liquids, can be placed on top of each other in frames of stainless steel, so that, for example, 90 pictures of the size 7.5 × 10 cm may be processed simultaneously. The developer tank is equipped with a motor-driven propeller and thermostat. Such an apparatus, which is supplied by several German manufacturers, is especially important for the treatment of Gevacolor prints, because the long duration of the processing renders the tray development tedious.

The capacity of prints per liter of developer depends on the permissible color shift. For high requirements 25 sheets of 9 × 12 cm can be assumed per liter of fresh color developer. With exhaustion there is a shift of the color balance towards cyan. For the shop this can be compensated by using a replenisher system. The same holds true for the negative process.

The drying of the prints is best achieved by air drying at somewhat increased temperature on frames covered with gauze. It is possible to press the pictures afterwards at a moderate temperature, to ferrotype them, again with little or no heat. Mounting on cardboard also can be done with adhesive foils, avoiding high temperatures, but increased pressure is harmless. Rubber solutions (caoutchouc) or neutral plastic adhesives (acrylate) may also be used. Any retouching is done with albumin glaze transparent colors.

Standard Viewing Light is Needed

The qualitative judgment of the color prints is an especially difficult task. This holds true for the general judging technique as well as for comparisons of the result obtained with the subject under consideration using the special properties of the various brands. Up to now a standard light source for judging the finished pictures has not been specified. This would be

most important; for the formed color shifts have to be compared with each other in unfiltered and filtered prints. It goes without saying that in a laboratory always the same light source is used for this purpose, but it would be desirable if everywhere the same standard source would be employed.

For example, if the resulting color prints are judged in average daylight, in fluorescent tube illumination of various color characteristics, and in tungsten light of medium intensity, and one judging immediately following each other, it is astonishing how very great are the apparent differences in the color balance. The fluorescent tube of about 6000K has proven so far the most satisfactory standard light source. It is being sold, for example, in Europe by Osram under the designation H.N.T.202 - 40 watt. Gevaert recommends another type of 7000K which, however, apparently leads to deviating results in the judging. When using incandescent lamps a Gevaert special blue filter CTB 16 is recommended.

A comparison of the color print with the original subject may show a satisfactory color reproduction of the original colors, yet a certain decrease of the brilliance as compared with a transparency. However, the loss of brilliance is considerably less than, for example, in Printon, which is a picture on a white cellulose acetate support according to the reversal process. With regard to the color reproduction compared with the subject it can be said that there is not much of an absolute correctness. However, we must remember that the color perception of the human eye too is very relative. It differs from one individual to another and depends to a great extent on outside influences—total brightness, subjective and objective contrasts. This subject has been dealt with many times in the scientific literature, and always the generally satisfactory character of the dyes obtained in the tripack by chromogenic development was established. One must therefore limit the problem to whether the color reproduction is sufficiently true to nature for the average observer. This is indeed the case if ideal conditions for the exposure illumination in relation to the sensitization of the negative material prevailed and the printing and processing techniques were observed properly. Another condition is that the negative and positive materials have not been stored too long or were faulty.

Even under these conditions the different brands produce very different results with an exposure of the same subject under the same lighting conditions. It can be stated generally that in Europe as a rule colors are preferred which are much more subdued, i.e. have less brilliance, than those fitting the American taste. During the course of their brief technical development, the European processes have repeatedly changed their overall character with regard to the keeping quality of the emulsions.

Fidelity of Agfacolor Prints

According to the present status we can say that a picture according to the Agfacolor process as a rule has a much softer gradation than that obtained with the other three processes. The color scale excels in purity, with the reservation that the chamois-colored paper background always confers a corresponding overall tint to the picture. In parallel there is an apparent intensification of the reproduction of yellow. The reproduction of this layer color is always somewhat problematical, because a pure lemon yellow, which would be ideal, so far could not be produced by chromogenic development. The purest yellow tones always show a certain shift towards orange, i.e. according to Ostwald 08. The purity of the magenta

layer color is very close to the theoretical value with all processes. However, they differ somewhat in their black content, which is quite small for Agfacolor. This influences the reproduction of cinnabar-red and yellow-green tones unfavorably. With regard to the cyan color too the theoretical value is almost reached, which here comprises a greater black content anyhow. The increase in brilliance on Agfacolor prints can be obtained by extension of the developing time within certain limits which are set mainly by the simultaneous increase of the background fog.

Appearance of Gevacolor Prints

The Gevacolor prints so far showed a somewhat higher black content compared with Agfacolor, but a better contrast and a better background black. Besides, the paper support is pure white or has a very light gray tint. The last-mentioned point must be considered an extremely important advantage.

The brilliance of the Gevacolor paper has been greatly improved for the recent emulsions, at the beginning of 1952, by changes in the color formers, with simultaneous increase of the contrast.

Telcolor and Ferraniacolor Print Quality

The color brilliance obtained with Ferraniacolor is comparable to that of the other brands. The purity of the whites is here excellent too, but not that of the darker image areas. There as a rule appears a brownish background tint, and this apparently is related to the mask processing of the negatives. With the Tellko process the brilliance in certain cases is perhaps even greater than with the other three, but for the purity of the whites and blacks the same holds true as for Ferraniacolor. The thin paper support differentiates this material from the others and introduces certain processing difficulties.

Fastness to Light

Finally the question of the fastness to light of the resulting color prints may be mentioned. Here the situation is not very satisfactory in any case, although it has been improved considerably in recent years. Experiments to achieve improvement by special ultraviolet-absorbing light-protective agents have not been particularly successful. It is therefore recommended to use current color prints only as album pictures or for exhibition purposes where they are not struck by sunlight. According to the present knowledge it is impossible by the technical method described here to obtain by chromogenic development dyes of greater light-stability. A reaction would have to be found which also begins with the reduction of silver bromide but does not employ derivatives of *p*-aminodiethylaniline as starting point so that dyes of other types with better fastness properties than the quinoneimide and azomethine compounds can be formed.

The enlargement limit can be assumed at 4 to 4.5 times. Beyond that magnification the graininess is disturbing on close viewing. The resolution of the relatively heavy layer systems (some thousandths of a millimeter), of course, is lower than that of normal negative layers; it differs from one brand to another. Black-and-white prints can be made from such color negatives in the usual manner.

From the standpoint of economics, we mention the following: The prices for negative film 120 amount here in Sweden at the present to 8 to 10 Swedish kronas, depending on the make (about \$1.50-\$1.80); the processing for this roll costs kr

5.75. The price for prints of postcard size also is kr 5.75, or about one dollar each. The costs in other European countries, as far as they have the possibilities for this photographic technique, are analogous.

It is apparent from this discussion that the described negative-positive technique is by no means very simple. The expert, therefore, finds it rather surprising that Agfa today still believes they will succeed in teaching this process to the photog-

rapher in a one week's course, and restricts the sale and use of its printing materials to participants of such a course. The other firms have no such restrictions. The negative material on the other hand, is obtainable everywhere in the free trade.

In conclusion we can say that the material for all four processes described here can be purchased at the present here in Sweden, but that the processes of Agfa and Gevaert have by far the widest distribution.

TWO-BATH FIXATION OF PRINTS*

J. I. Crabtree, R. W. Henn, and R. F. Edgerton

SUMMARY

When using two successive fixing baths, solubilization of the silver halide is accomplished in the first bath, while the second, relatively fresh bath, is used to wash out the complex silver thiosulfates formed in the first bath. It is these salts which decompose to form over-all stain on prints which contain residual silver; hence the useful life of a print fixing bath is largely determined by the silver content.

The accumulation of silver in the second bath is dependent upon (a) the silver content of the emulsion, (b) the amount of image developed, and (c) the rate of carry-over from the first bath.

It is customary to advance the relatively slightly used second bath at the end of each cycle to replace the first. This introduces more silver into the system on succeeding cycles, but equilibrium is soon reached with approximately a one-third increase in the silver content of the second bath.

The economy of two-bath fixation is considerable, it being possible to process 200 prints per gallon as against 50 in a single bath with the same final degree of print permanence.

IN A GENERAL WAY, photographic processing may be divided into two steps: (1) development of the exposed silver halide, and (2) removal of the unexposed silver halide. It is the intention of this paper to deal with an efficient method of removing completely the unexposed silver halide in order to avoid the over-all stains which occur when residual silver salts decompose in a print on storage or when prints are subsequently toned.

A fresh fixing bath removes the silver very efficiently, but as it is used, it accumulates more and more silver, which tends to be adsorbed by the gelatin and paper base and washes out only with great difficulty. The higher the concentration of accumulated silver in the fixing bath, the more difficult the washing problem becomes and, to insure full freedom from stain on subsequent toning or storage of the prints, the bath must be used for relatively few prints before it is discarded.

Crabtree, Eaton, and Muchler¹, in their comprehensive investigation of the fixing and washing process set this exhaustion figure as low as thirty 8-X10-inch prints per gallon and, in the case of the most exacting archival uses, as low as five 8-X10-inch prints per gallon. However, they point out that these low exhaustion figures, which are much less than those commonly employed in practice, may be greatly extended by the addition of a second fixing bath, which effectively washes the adsorbed silver out of the print. They show that two hundred 8-X10-inch prints may be processed through the two 1-gallon baths as compared with thirty prints through the single bath, and point out that further economy may be achieved by re-using the relatively slightly

exhausted second bath or advancing it to replace the first.

It has been the function of this investigation to consider the limitations which may be placed on the continued advancement of this second bath, to inquire into the effect of various emulsions and carry-over rates, and to recommend certain practical applications of the system.

Limitations to Re-Use of Fixing Bath

As pointed out above, in a two-bath fixing process, the first bath accumulates a considerable quantity of silver, which may be adsorbed to the print, while the second bath "washes" this silver from the print much more efficiently than is possible with water alone. One way of looking at this process is to think of the solubilization of silver as occurring through the formation of a double salt, $\text{Ag}_2\text{Na}_2(\text{S}_2\text{O}_3)_2$, which is the more soluble, the lower the silver content.²

While it is essential that the silver content of the second bath be kept low, the silver content of the first bath can become quite high without injuring the efficiency of the fixing process. Therefore, when the used second bath, containing a small amount of silver is advanced to replace the first, and a fresh second bath is substituted, the silver present in it will not materially affect its fixing properties.

It is seen, however, that as the silver content of the first bath increases the silver content of the second bath will increase also, since each print carries some of the bath with it. And whereas during the first exhaustion cycle the first few prints carry almost no silver to the second bath, silver will be carried over by even the number one print during the second exhaustion cycle. This

* Communication No. 1508 from the Kodak Research Laboratories. Received 18 August 1952.

will, of course, mean a higher rate of silver build-up in the second bath, and if it fixes a similar number of prints, it will have a higher final silver content than at the end of the first cycle. And if this bath is, in turn, used as the first bath in the third cycle, it will contribute still further to silver build-up of the new second bath. It is seen therefore that this problem of increasing silver content with successive exhaustions could form a severe limitation to the number of exhaustion cycles possible with a given system. To determine an answer to this problem, the following investigations and calculations were undertaken.

Re-Use: A Laboratory Exhaustion

1. Conditions

In the first series of exhaustion tests, quite severe conditions of processing were chosen. The emulsion selected was a portrait paper rich in silver (Kodak Platino Paper, grade G-3) on a double-weight stock which carried over a considerable quantity of fixer. However a 5-second draining period between baths tended to reduce this quantity, and the measured carry-over was 8 to 9 cc. per 8×10-inch sheet or slightly under 2.5 gallons per 1000 8×10-inch sheets. One-third of these were given a flash exposure and the other two-thirds were unexposed to approximate the exposure ratio in typical pictorial work. All were developed normally, passed through a stop bath, and then fixed 3 minutes in each of two successive baths of Kodak Acid Fixer. Control sheets were washed for 30 minutes at 65 F in a circular washer and

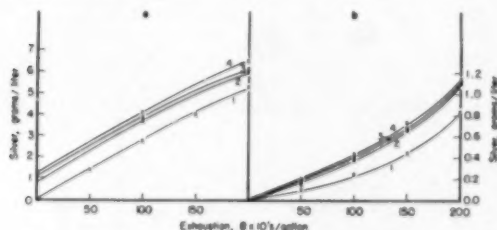


Fig. 1. Silver content of the fixer vs. degree of exhaustion. (a) First bath, (b) second bath. The second bath has been advanced repeatedly, the succeeding cycles showing progressively higher silver build-up. Note that the silver content of the second bath obtained during the third and fourth cycles is but little greater than that obtained during the second cycle.

tested for silver content. The "prints" were shuffled well in each bath and care was taken to keep the developer and stop bath fresh. One-quart quantities of each bath were employed, and a cycle was completed by the processing of fifty 8×10-inch prints through these solutions (equivalent to two hundred prints per gallon), and the second fixing bath was then advanced to replace the first. A total of four cycles were run.

In addition to the tests on the various prints, samples of fixing bath were taken at intervals. These samples were analyzed for silver by sulfide precipitation, using the Argentometer of Hickman and Weyerts³, but their procedure was modified by the addition of ethylenediamine tetracetic acid to prevent interference by other metals present. The results were in good agreement with those of selected samples analyzed by two other methods.

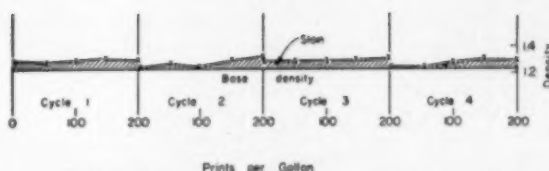


Fig. 2. Silver content of print. The residual silver in the print has been converted to silver sulfide and the transmission density of this stain has been plotted against the degree of exhaustion.

2. Silver Content of Fixers

The silver content of the fixing baths was plotted against the degree of exhaustion, as shown in Figure 1. Figure 1a applies to the first bath, Figure 1b to the second bath, while the "cycles" are indicated by numbers. Note the enlarged scale employed in plotting the silver values in Figure 1b. In the first cycle, when both baths are fresh, it will be seen that the silver builds up rapidly in the first bath, amounting to 2.2 grams per liter at eighty prints per gallon and in excess of 5 grams at two hundred prints. The silver content of the second bath builds up very slowly initially, and is only 0.25 gram per liter at one hundred prints. It increases rather more rapidly after this point, however, and amounts to about 0.9 gram per liter at two hundred prints.

Since this bath is then advanced to replace the first, at the beginning of the second cycle the first bath will have a silver content of 0.9 gram per liter. The carry-over of this silver into the second bath is noted in the increased rate (Curve 2) at which the silver builds up during the initial period and in the higher final value, amounting to about 1.1 gram per liter.

At the beginning of the third cycle, the silver content of the first bath has become 1.1 gram per liter, but this is not a great deal worse than during the second cycle and the increment of silver accumulating from this proved not to be very great at any time, and of the order of the experimental error (possibly 10%) on the completion of exhaustion. And the fourth cycle did little to increase the silver content further, virtual equilibrium having been obtained.

3. Stain

The potential stain, which might be produced on storage or on sulfide toning, by the residual silver in the prints, can be determined by bathing the print in sodium sulfide.⁴ The control prints were therefore treated in this manner, and the resulting densities read by transmitted light, using a blue-sensitive photocell to intensify the yellow-brown density of the stain. In Figure 2, these densities are plotted against the degree of exhaustion. The densities are very low, amounting to a maximum of only about 0.1 under these conditions and to not more than 0.02 by reflected light. This stain indicates a silver content of about 0.003 milligram per square inch and corresponds to a light cream tint on the print.

Factors Affecting Silver Accumulation

The exhaustion described above showed (1) the rapid arrival at equilibrium conditions, and (2) a one-third increase in silver content on successive exhaustions. However, there are many variables which affect this

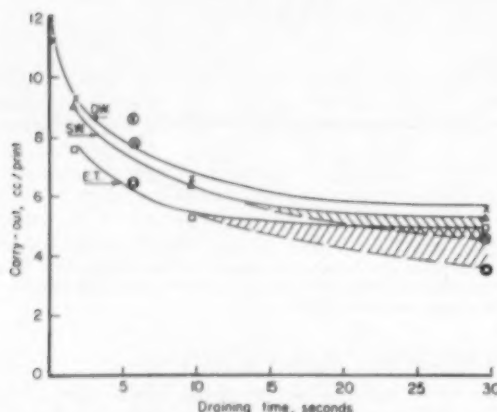


Fig. 3. Carry-out of various papers as a function of the draining time. The circled data apply to 8-x10-inch prints drained individually, the other data to prints drained as clumps of twelve. The data are for double-weight (DW), single-weight (SW), and extra-thin (ET) papers. The shaded areas show the reduction in carry-out obtained by individual draining for long periods.

equilibrium. It has been mentioned that the silver content of the second bath will be dependent on the rate at which the first bath is carried over into it. It will also depend on (a) the silver content of the emulsion, (b) the amount of this silver that has been developed, and (c) the number of prints fixed.

1. Carry-Over Rate from First to Second Bath

(a) *Measurement.* The quantity of solution carried over by each print will depend both on (1) the thickness of the print, and (2) the time of draining.

The solution carried over by a print is both that absorbed in the emulsion and the base and that adhering to the surfaces. Most of the surface fixer and some of the absorbed fixer will drain off from the print when suspended over the bath. Figure 3 gives data obtained with various draining times. These prints were first developed and fixed normally, and then drained (1) individually, or (2) in clumps of twelve. Double-weight, single-weight, and extra-thin papers were employed, and draining times ranged from 2 to 30 seconds. The largest effect was produced in the initial draining period, when the surface hypo ran off rapidly, and little difference was obtained between prints drained individually and prints drained in clumps. This has practical implications, since it is generally more convenient to drain the prints in clumps. However, some advantage is obtained by individual draining for long periods of processing (see dotted lines).

These measurements show a range of carry-out figures varying from 3.5 to 12 cc. per 8-x10-inch print, depending on the weight of the paper and on the time of draining. Measurements made in commercial processing plants have also given carry-out values as high as 12 cc. per print. But if the draining time is limited to the range of 5 to 10 seconds, the carry-out is restricted to 5.5 to 8.5 cc. per print.

(b) *Calculations at Various Carry-Over Rates.* If the carry-over rate is known, and assuming that the fixer adsorbed by the print and that in the bath are at equilibrium, it is possible to calculate the content of any of

the baths at any time. And if the silver content of the print is known, absolute values of silver in the fixer may be achieved. The equations used for these calculations are those of Herzberger and Henn,⁵ which give the content of the first fixing bath as:

$$B = \frac{1}{(1+K)^n}; \text{ and } A = 1 - B,$$

while the content of the second bath is given by:

$$C = \frac{1}{(1+K)^n}; B = \frac{1-(1-K^2)^n}{K(1+K)} 2n; A = 1-(B+C).$$

In these equations, the carry-in rate, of the diluents, A , into the first fixer, B , and of this fixer into the second fixer, C , is given by K , while n is the number of prints processed.

We are chiefly interested in component A , which not only measures the carry-in of the preceding solutions (developer and stop bath), but also measures the silver, since each print will carry in unfixed silver halide as well as solutions. For example, an 8-x10-inch print might bring in 10 cc. of liquid and 0.1 gram of silver, to be fixed. It is convenient to think in terms of each 10 cc. of A containing this amount of silver, so that 1000 cc. would contain 10 grams of silver. In the general case, the silver content of the fixer will be proportional to A/K .

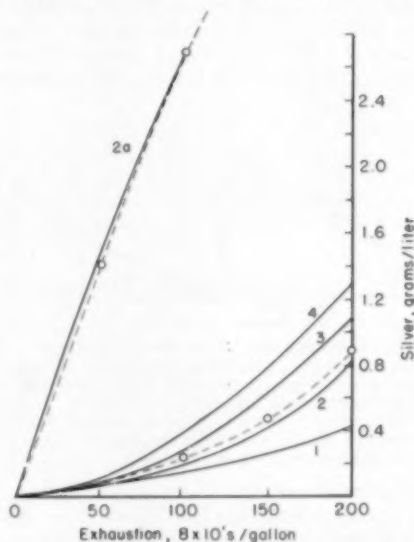


Fig. 4. The accumulation of silver in the fixing bath as a function of the degree of exhaustion and carry-over rate. Curves 1, 2, 3, and 4 apply to the second bath and to carry-over rates of 1, 2, 3, and 4 gallons per 1000 8-x10-inch prints. Curve 2a applies to the first bath and a carry-over rate of 2 gallons per 1000 prints. The dotted lines indicate the experimental data obtained from Fig. 1 and a carry-over of about 2-1/4 gallons per 1000 prints.

Figure 4 is based on calculations made according to these equations and a silver content of slightly under 0.1 gram per print. The numbers indicate the carry-over rate in terms of gallons per 1000 8-x10-inch prints. Several aspects of these curves are worth noting, namely: (1) The importance of the carry-over rate on the silver

Table I

EQUILIBRIUM COMPOSITION OF FIXER

Gallons per 1000 Prints*	Carry-Over, K, K	Composition, %		Equilibrium A ∞ , %	Increase A ∞ / A ₁
		After First Cycle A ₁	B ₁		
1	3.75	1.5	16	1.8	1.19
2	7.5	6	27	8.2	1.37
3	11.25	12	32	17.6	1.47
4	15	19	36	29.7	1.56

* 8-X10-inch prints.

content of the second bath—for example, at one hundred 8X10's per gallon the silver content varies from 0.40 to 0.14 gram per liter, and much of this variation could be achieved merely by adjusting draining times. (2) The marked advantage of two-bath fixation over single-bath operation, as shown by the steeply rising curve, 2a. (3) Good agreement of experimental and calculated values. This is shown by the inclusion of curves from Figure 1, which have been replotted here as dotted lines. The measured carry-out rate was slightly under 2.5 gallons per 1000 prints.

2. Repeated Cycling

The condition of the fixers during the succeeding cycles, the used fixer being advanced each time, can also be approached mathematically. In this case, let A_1 represent the fraction of stop bath, developer, and silver carried into the second fixer during the first cycle, and let B_1 represent the fraction of the first fixer carried in. During the second cycle, when the used fixer containing A_1 is employed as the first bath, the carry-in of component A will be increased by the fraction A_1B_1 , and on succeeding cycles the composition of the bath will be as follows:

$$A = A_1 (1 + B_1 + B_1^2 + B_1^3 + B_1^4 \dots),$$

or at equilibrium, when the number of cycles is large,

$$A = \frac{A_1}{1 - B_1}.$$

Since the higher powers of B become insignificantly small, equilibrium is reached quite rapidly, as shown in the plots of Figure 5, where little increase in silver content is obtained after the third or fourth cycle. Note again the close correspondence of experimental and calculated values. The dotted line (Curve A) is from the data of Figure 1, while the dashes (Curve B) are from an independent run under similar conditions but with a carry-out rate of about 12 cc. per print or slightly over 3 gallons per 1000.

Table I gives the limiting values of the increase, as obtained from the above equation. This varies from 19 to 56%, according to the carry-in rate. The larger increase obtained for high values of carry-over, K , is due to a corresponding increase in B_1 and the consequently greater significance of its higher powers.

These calculations and experiments show the effect of a high carry-over rate on the silver content of the second fixer to be twofold: (1) It results in higher build-up in the first cycle, and (2) the increase on recycling is greater. Table II, in which both these fac-

tors have been considered, is of practical use in this connection. Note the reduction in silver content of about one-third by the introduction of even a short draining period. This advantage could be used either as (a) an improvement in quality, or (b) a longer exhaustion life (about 20%) for equal quality.

3. The Unfixed Silver Halide

This will depend both on the original silver halide content of the emulsion and on the quantity which has been developed. The Platino paper used in these exhaustions was selected for its high silver content, while the exposure of one-third of the area duplicates most pictorial and portrait subjects. Figures 1, 4, and 5 and Table III are based on this rich emulsion and one-third exposure. The data may be applied to other emulsions and exposures, by adjusting the ordinates by the following factors:

Table II

EFFECT OF CARRY-OVER RATE

Carry-Over, K Gallons per 1000 Prints*	Cc. per Print	Condition	Silver Content (Grams per Liter)	
			First Cycle	Equilib- rium
3	11-12	Double-weight papers, mini- mum drain	1.08	1.58
2.5	9-10	Thin papers, no drain; heavy papers, 2 sec. drain	0.96	1.35
2	7-8	Most papers, 5 to 10 sec. drain	0.80	1.10
1	4-5	Thorough draining, thin papers	0.40	0.50

* 8-X10-inch prints.

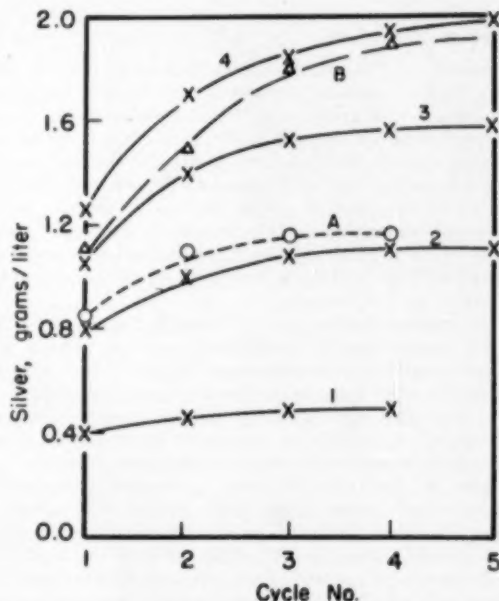


Fig. 5. The final silver content of the second fixing bath is plotted as a function of the number of cycles. Curves 1, 2, 3, and 4 apply to carry-over rates of 1, 2, 3, and 4 gallons per 1000 prints; Curves A and B to experimental exhaustions and carry-over rates of 2-1/4 and 3-1/4 gallons per 1000 prints.

Limitation of Fixer Life

1. Loss of Acidity

If an alkaline developer is carried into an acid hardening fixing bath, the acidity of this bath decreases with the following end results: (1) the fixer may no longer stop development rapidly and stains may be produced; (2) the hardening action is lost; and (3) the fixer may sludge. In the case of a strongly acid fixing bath, such as Kodak Fixing Bath F-5, and a dilute developer, such as Kodak Developer D-72 (1:2), serious loss of acidity occurs only when 30 cc. of developer are carried in per 100 cc. of fixer, which will give the bath a minimum exhaustion life of over one hundred 8- \times 10-inch prints per gallon. This value will be greatly reduced however for the less acid Kodak Fixing Bath F-6, and the use of this fixer is not recommended without a stop bath. But in modern processing, an acid stop bath is very commonly employed, so that loss of acidity is not ordinarily the limiting factor in the life of the fixer.

2. Dilution

As the fixing bath is used, it becomes diluted with the stop bath and the developer. Hypo concentration is lowered, increasing the fixing time. However, this dilution occurs relatively slowly, and even at the maximum carry-in rate described the bath will be diluted by only about 30% after processing one hundred 8 \times 10's per gallon and by about 50% at 200 prints per gallon. In a two-bath system, the hypo concentration in the second bath would still be high and the fixing action effective.

3. Silver Accumulation

Probably the most serious limitation to the life of a fixing bath, particularly when a stop bath is employed to maintain the acidity, is the accumulation of silver. The preceding paragraphs have revealed (a) the factors affecting the accumulation of silver, (b) the advantages of two-bath fixation in keeping the silver content low, and (c) the magnitude of the increase in silver content caused by the repeated advancement of the second bath. But in order to establish practical limitations on the use of the bath, the maximum tolerable silver content of the fixer must be determined.

The effect of the presence of silver in the fixing bath is to (1) increase silver retention in prints, which will cause over-all stain on prolonged keeping or on toning, and (2) increase hypo retention by the prints, which results in toning and "fading" of the image. Contrary to a popular impression, moderate quantities of silver in the bath do not appreciably increase fixing time.

Figure 6 illustrates the effect of increasing concentrations of silver in the fixing bath (Kodak F-5), added as silver bromide. These data differ from those obtained by Crabtree, Eaton, and Muchler, in that the acidity of the fixer has been maintained, whereas in their exhaustions no stop bath was used and the loss in acidity of the fixer overcame the effect of the added silver to a large extent. Note the increase in both silver and hypo. These data were obtained with Kodak Velox Paper, F-3, single-weight, fixed for 10 minutes, and washed for 30 minutes in cold (40 F) water. The hypo was de-

Table III

UNFIXED SILVER

Factor	Application
1.0	Rich portrait papers, high-speed industrial papers.
0.5-0.6	Most contact and projection papers.
0.5	Negative work, mostly black.
1.3	Positive line work, little black.

terminated with the silver nitrate test, the silver with sodium sulfide, and the values were assigned according to the published curve.⁴

(a) *Maximum Acceptable Silver Content of Fixer.* The acceptable silver content of the final fixing bath was set as low as 0.3 gram per liter by Crabtree, Eaton, and Muchler, who were interested in very low stain levels. They obtained this figure in an exhaustion of two hundred 8- \times 10-inch prints per gallon (single cycle). But in the example of Figure 1, owing to differences in emulsion and carry-over, the silver content was 0.85 gram per liter on the first exhaustion and increased to approximately 1.2 grams per liter on recycling. However, the stain level produced by the 1.2 grams of silver was not heavy and even at the 1.8 grams obtained in the one example of Figure 5, it bordered on acceptability.

(b) *Corresponding Degree of Exhaustion.* The silver content of the second bath of a two-bath system, after the fixing of two hundred 8- \times 10-inch prints and recycling, is ordinarily no more than half that of a single bath which has fixed the usually recommended number of 100 prints per gallon. Tentatively, therefore, a figure of two hundred 8- \times 10-inch prints per gallon (more precisely, two 1-gallon baths) would appear very reasonable for two-bath practice. This figure could be modified to adapt it to the several factors controlling silver content described above, which would vary the exhaustion between 175 and 250 prints per gallon. Also, about one-third more prints might be fixed during the first cycle than during successive cycles. However, the savings created in these

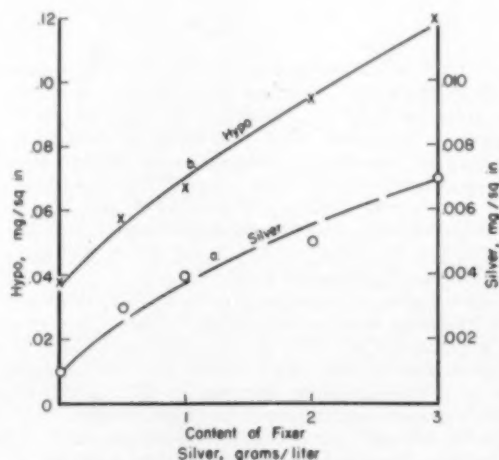


Fig. 6. (a) Hypo and (b) silver content of the print as a function of the silver content of the fixing bath. Note how both the hypo and silver retained in the print increase with the silver content of the fixer.

variations would commonly be offset by the inconvenience of determining and employing variable exhaustion figures.

4. Contamination and Error

The dangers of cumulative errors in replenishment, and of accidental contamination, ordinarily limit the life of continuous-use systems as much as any actual chemical change. In this case, the bath is dumped entirely after 400 prints have been fixed (200 as the second bath and 200 as the first bath), which limits the errors introduced by possible contamination, dilution, evaporation, overwork, etc., to those two cycles. However, sludges and scales or slimes may form in the trays or tanks, being removed only when the whole system is dumped and cleaned. This operation should consequently be performed at fairly frequent intervals, say after every 5 cycles. If sludging occurs in a bath, it should be discarded immediately rather than wait for the completion of the cycle. The volume of the bath should occasionally be checked for losses by evaporation and if these are appreciable, the level may be restored by adding water.

Practical Aspects of Two-Bath Fixation

1. Practical Use Tests

This analysis of the data would indicate as a reasonable system the use of two successive fixing baths exhausted to two hundred 8- \times 10-inch prints per gallon, with repeated advancement of the second bath, and a 5-second draining period between baths, of either single prints or clumps of prints.

The proposed system was therefore given practical use tests in two print-finishing establishments. The physical setup of installation No. 1 is pictured in Figure 7. Note the elevation of the second hypo tray and the faucet to allow easy advancement of the solution. Each of the trays held 5 gallons of fixer. A rocking device agitates the prints, making manual separation unnecessary. Finisher No. 2 used two 6-quart trays and advanced them manually.

The data obtained from these two finishers are entered in Tables IV and V. The higher silver content

obtained by finisher No. 1 is to be explained by the longer cycle he employed (up to 250 prints per gallon as compared with 167 for finisher No. 2), and a high percentage of line work on Kodagraph Projection Paper (silver factor, 1.3, Table III). Even so, the highest silver content obtained (1.6 grams per liter) probably does not exceed the upper limits of safety, while at the recommended exhaustion level the silver stayed below 1.25 grams per liter.

Table IV

FINISHER NO. 1				
Week	Day	Total Prints (As No. of 8 \times 10's per 5 Gal.)	Silver Content (Grams per Liter)	
			Bath No. 1	Bath No. 2
1	1	170	0.7	0.01
	2	415	1.25	0.25
	3	645	2.00	0.65
	4	798	2.20	0.85
	5	834	2.50	0.95
2	4.1	1.6
3	2.8	1.2
4	2.6	0.4
5	1	456	1.5	0.25
	2	667	2.4	0.6
	3	795	2.6	0.8
	4	965	2.8	1.2
	5	1260	3.2	1.6

Table V

FINISHER NO. 2			
Cycle*	Fixer Bath	Analysis	
		Silver (Grams per Liter)	Hypo (Grams per Liter)
1	1st	2.37	176
	2nd	0.60	209
2	1st	2.44	140
	2nd	1.26	224
3	1st	1.94	136
	2nd	0.68	209
4	1st	3.56	158
	2nd	0.66	201
5	1st	3.22	158
	2nd	0.50	210

* Cycle = Two hundred fifty 8- \times 10-inch prints through two 6-quart baths.



Fig. 7. A two-bath fixer setup. The 5-gallon trays of fixer are positioned at different levels, while a tap allows draining of the second fixer into the first. The motors activate rockers which insure separation of the prints during fixing.

The practical utility of a system is determined not only by the quality obtainable, but also by its convenience. Neither of these finishers (nor three others who made a partial test of the system) found the demands excessive, and the drain period, while not previously practiced by the workers, did not delay production when the prints were handled in clumps of 10 to 20 and then separated on immersion in the next bath. Some operators, particularly those processing prints of varying sizes, found accounting difficult and preferred measuring the silver content of the fixer (see below).

A related, although not strictly parallel, application of multiple-bath fixation is obtained in the continuous paper processor of the photofinisher. Here a counter-current system is maintained, which replenishes the last bath continuously and flows this into the preceding baths. Thus, in a three-bath system, the successive silver concentrations, at equilibrium, were found by

Messrs. Pardee, Spelbrink, and Woodward, of this Company, to be: 1.45, 0.36, and 0.12 grams per liter. The washing time is very brief in such a processor, and in order to keep the silver content of the last bath, and of the print, particularly low, an additional fixing bath with a high rate of fixation is now employed as a stop bath, reducing the silver concentration of the final bath to 0.04 gram per liter.

2. Measurement of Silver in the Fixer and in the Print

In some cases, as mentioned earlier, it is inconvenient to keep a record of the number of prints processed, and a more direct measure of the condition of the fixer is desirable. The test solution "B" of the Kodak Testing Outfit for Stop Baths and Fixing Baths may be employed for this purpose. When used as directed for a print fixing bath, 5 drops of the test solution are mixed with 5 drops of water and 10 drops of fixer are added. This causes a definite cloudiness when the silver content of the fixing bath is slightly over 1.0 gram per liter, or somewhat less, if the bath is dilute. This is consistent with the above conclusions, which placed the safe silver content of the fixer at a value of 1.0 to 1.5 grams per liter.

A further check, which also includes the thoroughness of the wash, is to test the final prints for hypo and silver. These procedures, along with a suitable comparison scale, are included in a Kodak leaflet,⁶ and are described in some detail in Reference 4.

3. Economics of Two-Bath Fixation

The principal object of two-bath fixation is to produce prints of a high degree of permanence and stability. But it may result in considerable chemical savings as well.

Typically, a single bath that has fixed 30 prints will have accumulated as much silver (0.9 gram per liter Fig. 1) as the second gallon of a two-bath system after fixing 200 prints—that is, doubling the quantity of chemicals has resulted in a sixfold increase in capacity. And a still greater chemical savings is accomplished if the bath is re-used.

However, a gallon of a single fixing bath is not usually used to fix thirty or forty 8×10-inch prints, but for 100. The cost of two 1-gallon baths used to process 200 prints, of course, equals that of one 1-gallon bath used to process 100 prints. But the silver content of the last bath of the two-bath system will be only one-third that of the single bath, greatly improving potential print stability. Then if the second bath is re-used, chemical savings of one-third to one-half are realized, with the silver content still no more than half that of the single bath. The two-bath, recycling system can therefore mean "twice the quality at half the cost."

Recommendations

The following system of two-bath fixation is recommended as an economical and practical aid to obtaining high print permanence and freedom from stains on toning:

1. Following normal development and immersion for at least 30 seconds in an acid stop bath, the prints are fixed for 3 to 5 minutes in each of two successive fixing baths.

2. The prints are drained, either singly or as a clump, for a period of 5 seconds (or longer) before immersion in the first fixing bath, between fixing baths, and following the last fixing bath. Of these, the draining operation between the first and second fixing baths is particularly important.

3. The prints are separated well on immersion in each fixer and at intervals during fixation.

4. Following final fixation, a normal washing procedure is employed. This comprises 30 minutes (single-weight prints) or 60 minutes (double-weight prints) in running water at 65 to 70 F, changing at the rate of 12 times per hour. A hypo eliminator, such as the Kodak Hypo Eliminator HE-1, or a washing accelerator like a Kodak solution may be used advantageously where more rapid washing or great permanence is desired.

5. In a system employing two 1-gallon fixing baths, the first fixer is discarded following the processing of two hundred 8×10-inch prints. The second bath is then moved over to become the first bath and a fresh gallon of fixer is used for the second bath. Proportional exhaustion figures are used for other quantities of fixers and other sizes of prints. For example, two hundred 4×5-inch prints are fixed in two 1-quart baths, eighteen hundred 2½×3½-inch prints in two 1-gallon baths, etc.

6. The system should be completely dumped and cleaned after each five cycles, i.e., after one thousand 8×10-inch prints have been processed in the two 1-gallon fixing baths. The processing of two hundred prints per gallon, followed by advancement of the second bath, might conceivably be repeated indefinitely without excessive silver build-up in the second bath, provided the carry-over rate were low and contamination were avoided. However, because of the rigidity with which these two precautions must be observed, it is simpler in actual practice to discard the entire system after five cycles.

7. Alternative to keeping count of the area of prints processed, or supplemental to such accounting, the change point may be determined by using the Kodak Testing Outfit for Stop Baths and Fixers to test the second bath.

8. When a single fixing bath is employed, comparable quality cannot be maintained if more than fifty 8×10-inch prints are fixed per gallon. However, quality acceptable for many commercial purposes may be obtained when 100 prints are fixed per gallon, provided washing is thorough.

References

1. Crabtree, J. I., Eaton, G. T., and Muehler, L. E.: The Removal of Hypo and Silver Salts from Photographic Materials as Affected by the Composition of the Processing Solutions, *J. Soc. Mot. Pict. Eng.* 41: 9-68, 1943.
2. Bassett, H., and Lemon, J. T.: The System $\text{Na}_2\text{S}_2\text{O}_3\cdot\text{Ag}_2\text{S}_2\text{O}_8\cdot\text{H}_2\text{O}$ at 25° C, *J. Chem. Soc.* pp. 1423-1427, 1933.
3. Weyerts, W. J., and Hickman, K. C. D.: The Argentometer—An Apparatus for Testing for Silver in a Fixing Bath, *J. Soc. Mot. Pict. Eng.* 25: 335-340, 1935.
4. Crabtree, J. I., Eaton, G. T., and Muehler, L. E.: A Review of Hypo Testing Methods, *J. Soc. Mot. Pict. Eng.* 42: 34-57, 1944.
5. Henn, R. W., and Herzberger, M.: Equations for Calculating the Condition of Photographic Solutions in Continuous Systems, *PSA Journal* 13: 494-497, August, 1947.
6. *Permanence of Photographic Negatives and Prints*. Booklet available on request from Sales Service Division, Eastman Kodak Co., Rochester 4, N. Y.

PHOTOGRAPHIC STANDARDS FOR CAMERA SHUTTERS

Vernon E. Whitman*

FOUR AMERICAN STANDARDS providing for uniformity of calibration and performance characteristics of camera shutters were approved by the American Standards Association December 23, 1952. These deal with both focal-plane and between-the-lens shutters used with still picture cameras. This national recognition of an agreement reached by American photographic interests—producers, consumers, distributors, general-interest groups—represents a decisive forward step out of the doubt, controversy, and *taboo* in which the subject has for so long a time been shrouded. The Photographic Society of America participated in that achievement.

Titles of the four new standards, which are available from the American Standards Association, Incorporated, 70 East 45th Street, New York 17, New York, are as follows:

PH3.2-1952 *American Standard Method for Determining Performance Characteristics of Focal-Plane Shutters Used in Still Picture Cameras*. Eight pages; price, thirty-five cents.

PH3.3-1952 *American Standard Exposure-Time Markings for Focal-Plane Shutters Used in Still Picture Cameras*. Leaflet; price, twenty-five cents.

PH3.4-1952 *American Standard Method for Determining Performance Characteristics of Between-the-Lens Shutters Used in Still Picture Cameras*. Eight pages; price, thirty-five cents.

PH3.5-1952 *American Standard Exposure-Time Markings for Between-the-Lens Shutters Used in Still Picture Cameras*. Leaflet; price, twenty-five cents.

History of the Shutter Project

These four American Standards resulted from approximately ten years of cooperative effort on the part of the leading manufacturers and some of the best informed users of such equipment in the United States. The project was initiated by the U. S. Armed Forces in the early 1940's as one of the many clarifications deemed necessary to efficient pursuit of the war effort. Brought to the American Standards Association for development under their voluntary program for national standardization, the project was turned over to War Standards Committee on Photography and Cinematography Z52 under the Chairmanship of Mr. Robert B. Shepard of the War Production Board. Two of the shutter standards projects became American War Standards in 1946 and the other two were in the status of "Proposed American War Standards" when hostilities ceased and the war standards program ended.

The Sectional Committee on Standards in the Field of Photography, ASA Z38, took up the shutter standards projects under general practices of the American Standards Association to review all temporary War Standards for possible adaptation to peacetime use. When Sec-

tional Committee Z38 was disbanded late in 1950, the projects were assigned to the new ASA Sectional Committee PH3 on Photographic Apparatus under the Chairmanship of Mr. Frank E. Carlson, APSA, Hon. PSA. Active work of reviewing the previous work and translating the wartime projects into civilian standards was done by Subcommittee PH3-1 of which the writer was Chairman.

Organizations in addition to the PSA that have constructively contributed to these new American Standards for camera shutters and have agreed to their provisions include U. S. Departments of the Air Force, the Army (Signal Corps), and the Navy as well as the National Bureau of Standards, Ansco, Bolsey, duPont, Kodak, Fairchild, Graflex, and optical interests including American Optical, Bausch & Lomb, Ilex, E. Leitz, Wollensak, Carl Zeiss, and the Optical Society of America.

Basic Considerations and Scope

As an illustration of the underlying principles that apply to the development of all American Standards, the following considerations were recognized by Subcommittee PH3-1 as that group wrestled with the draft proposals for shutter standards handed down by the predecessor committees:

1. The standards could not be drawn to the advantage of any single manufacturer or group (as through recognition of a detail covered by an existing patent).

2. The standards must not stipulate dimensional tolerances or performance requirements attainable only on a laboratory or model shop basis but instead must be consistent with proven design and precision mass production techniques.

3. The standards should not include material that would be restrictive of future progress or development (such as might result from stipulations governing weight, size, shape or materials of construction).

4. The standards should not be either textbooks on design, manuals of operation, or treatises on testing but should be engineering documents plainly setting forth the technical requirements in a complete and lucid manner consistent with the understanding of workers conversant with this field of mechanics.

5. The standards were also limited by the Scope of Sectional Committee PH3, under ASA rules, to exclude shutters used on motion picture cameras. By mutual consent of the committee members, the present standards were specifically limited to shutters for still-picture cameras, omitting aerial cameras.

A discussion of the considerations faced by the Committee was prepared and circulated to the members of the ASA Photographic Standards (Correlating) Committee for their guidance in evaluating the work of Sectional Committee PH3. The following excerpts are taken from that document.

For those who have not been privileged to carry this project to its present phase, the following notes typical of the considerations involved in securing the support of one or more of the cooperating factions will

* Graflex, Inc., Rochester, New York. Chairman of Subcommittee PH3-1 on Shutter Standards of the American Standards Association. Received 20 November 1952.

indicate the thoroughness with which all manner of possibilities were tried before coming to agreement on the proposals here submitted for your evaluation.

1. *What Speed?* The basic question as to whether shutters should be marked in "total open time" or "effective exposure time" required a decision as to the relative importance, in this standardization, of certain Armed Forces criteria as compared with the convictions and experience of established commercial interests. The former stressed motion stopping ability; the latter, normal photographic practice and consistency with accepted exposure measuring devices. Although the test procedures outlined in the relevant proposals give both performance figures, agreement that these standards should relate to commercial items not primarily intended for aerial photography resulted in the choice of "effective exposure time" for the speed markings specified.

2. *Speed Scales.* At the beginning of this standardization project a real opportunity appeared to present itself to make obsolete most of the weird numbers which had appeared on shutters of the past and for starting off fresh with a series having some theoretical justification. Such a scale, having a constant ratio of 2 to 1 between adjacent numbers, promptly gained the support of the technically trained committee members. On the other hand, the manufacturers (and especially their sales departments), whose approval would be necessary for any standardization, were convinced that any departure from their long established numbering systems would confuse the users of their equipment and, therefore, as a practical matter, completely outweigh the advantages of the theorists. Hence, the duplicity of scales found in the focal-plane shutter standard.

3. *More Accuracy?* The tolerances on effective exposure time, which form a basic part of the proposals concerned with exposure-time markings, represent the best commercial possibilities under existing and foreseeable conditions of design and manufacture. The devices to which these standards apply are not primarily precision time interval measuring devices. They have been proven in practice to be capable of the best photographic results ever secured. To make them more accurate for specialized technical applications would result in cost increases considered completely out of proportion to the photographic benefits which would result.

4. *How Cold?* The Armed Services, as important contributors to this entire standardization project, need equipment which not only operates at temperatures below -40 Centigrade but also at "room temperature." For such applications, special specifications must apply not covered by these performance standards which, again, are primarily related to good commercial practice. To guarantee these tolerances over a wider range of temperatures would involve disproportionate disadvantages to the average professional and amateur user.

5. *Low Efficiency?* Although efficiency is carefully defined and its measurement outlined in these proposals, no lower limit has been set for its acceptable value. In view of the relationship between efficiency and the effective exposure-time markings, this omission has appeared to some as a temptation or invitation to produce still less efficient shutters in order to gain thereby a higher marked top speed. According to some designers, however, this temptation may find an automatic economic deterrent, especially in the case of between-the-lens shutters. For either type of shutter, it has been obvious that continuing good product reputation will not be enjoyed by a manufacturer who succumbs to this temptation. On the other hand, in the present state of the art, shutter standardization will be materially delayed if it must be predicated upon agreement as to the lower acceptable limit on efficiency. It may be better sought as a possible future revision in the standards as now proposed.

6. *More Methods?* It will be obvious to those skilled in such matters, that other methods of measurement are equally applicable. These are allowed without violating any of the standard proposals as long as they give the equivalent figures within the accuracy needed. Not aiming to be a textbook on methods of measurement, these standards have, therefore, limited themselves to a single test method to be best suited for the purpose in the opinion of those who drew these documents together.

These four proposed shutter standards are, therefore, admitted compromises and as such cannot be expected to comply with the full academic requirements of all who may have occasion to study them. As practical documents, however, in a field urgently needing standardization, they are known to be great steps forward. It is the sincere hope of all who have cooperated in this effort that the balloting now in process will recognize this fact.

In the standards will be found definitions for a minimum number of terms important to universal application of the standards. Test procedures are specified that are acceptable for measurement of the necessary quantities.

Performance tolerances have been agreed upon that are consistent with good design and production practices.

Definition of Terms

Only four quantities have been defined: Total Open Time, Efficiency, Effective Exposure Time, and in the case of between-the-lens shutters, their Maximum Opening. Although an infinite variety of other wordings could have been adopted, and many of them were considered, those finally incorporated were accepted on the basis of maximum clarity consistent with good usage. Most important they give a common language for the measurement and evaluation of those derived values which are more important to the ultimate user: the utility, accuracy, and reliability of a camera shutter as a photographic exposure determining device.

Effective Exposure Time, as defined in these documents, specifies the time scale to be used in marking those shutters (focal-plane as well as between-the-lens) complying with the requirements of the American Standard. The same exposure meters and years of experience in taking pictures can now be used interchangeably between the two types of shutter.

Application of the Standards

As with all American Standards these four relating to camera shutters are purely optional in their use. They are in no sense mandatory unless adherence to them is specifically advertised or contracted for directly between purchaser and seller. As far as the photographic public is concerned therefore, until some manufacturer publicly affirms that his particular shutter complies with one of these standards, there is no implication that shutters not so specifically identified bear any relationship with these published standards.

Also in common with all other American Standards, these are live documents and come up for review automatically every three years, or sooner if the need becomes apparent. At that time, they may be reaffirmed, revised, or completely withdrawn. In that way standards spell progress.

NEW MOTION PICTURE STANDARDS

Two new American Standards in the field of motion pictures, developed by the Society of Motion Picture and Television Engineers through their engineering committee activities have been approved as American Standards and are now available. They are PH22.38-1952 (Revision of Z22.38-1944) "Raw Stock Cores for 16mm Motion Picture Film" and PH22.83-1952 "Edge-Numbering 16mm Motion Picture Film."

The first Standard concerns the specifications and recommended dimensions for cores (without flanges) on which 16mm motion picture raw stock is wound while the second establishes a uniform practice with respect to the interval between edge numbers when they are latent-image printed on 16mm raw stock film. This distance has been established as 40 frames between consecutive numbers. It is not the intent of this standard to imply that all 16mm film should be edge-numbered. Both standards are available from ASA headquarters, price twenty-five cents each.

K. SHAFTAN

SUBMARINE PERISCOPE PHOTOGRAPHY

J. C. Milligan*

UPON THE COMPLETION of the first modern submarine periscope it must have been apparent that the instrument could be used for photography. It was not until more recent years, however, that serious attempts in that direction were made. The advent of modern high-speed negative materials was of prime importance in making submarine periscope photography practical, although reasonably good photographs had been made by the Kollmorgen Optical Corporation in 1928. From that time on, considerable developmental work was done and, as early as 1940, some operating submarines began to carry camera equipment. During the years 1940 to 1942, a number of GSAP and standard motion picture cameras were modified for use on submarine periscopes.

In order that the photographic problem may be better understood, it is necessary to briefly describe a submarine periscope. Physically, the instrument is a piece of pipe or a tube measuring from thirty to fifty feet in length, and usually having an outer diameter of from six to nine inches. Optically, it may be a simple telescope with head and eyepiece prisms, or it may be a series of complex components serving as the heart of the submarine fire control system. Needless to say, the tube containing the optics must be hermetically sealed, since it spends considerable more time under the water than above. It is not surprising that an instrument combining the above characteristics with sufficient ruggedness to withstand the pressure of deep submergence, as well as the shock of depth charge explosions, will weigh from one to two tons.

The eyepiece of the periscope, when the instrument is extended, is located in the conning tower of the submarine, where space is critically limited. It is here that many of the instruments and devices required in maneuvering and navigation, and in making an attack, must be located. When all of this equipment and the five or six men needed to operate it are assembled in a space that is perhaps six by fifteen feet in size, there is certainly little room for cameras and a photographer. This lack of space is accentuated by the fact that there must be hatches opening to the control room below and to the bridge above, in addition to wells for the two periscopes to retract into. These wells further complicate photography since they cannot accommodate the cameras, and the cameras must be removed each time the periscope is lowered.

Two classes of still photography are of concern to submariners, and each has its own peculiar problems. The first is simple record photography, in which case the submarine may be required to record, on film, all shipping encountered, or, in time of war, it is highly desirable to photograph each target. In this case, the problem of photography is complicated by the fact that the photographs must be made by the submarine skipper, who has hundreds of operational and tactical problems and decisions to face during a single attack. Further, the

skipper is a highly trained and extremely active military man who has little time to become familiar with photographic equipment or procedure. Therefore, camera equipment must be simple and reliable in operation and must, above all, be capable of being instantly disposed of. Usually the skipper will not have the benefit of professional photographic advice, since, under ordinary circumstances, a submarine cannot accommodate personnel who are not essential to its operation and safety.

In the case of reconnaissance photography, the problem is different, in that specially trained personnel will be available for photography; or, if the photographs are made by the skipper, he will have the benefit of professional advice. However, in this case, the photographic requirements are much more exacting. If the photographs obtained are to have any real value for intelligence purposes, it is necessary that they be of good



Fig. 1. Target vessel photographed through a submarine periscope with the LSI-880 at fairly close range. The MK 4 camera was used.

quality, particularly with respect to resolution. It is oftentimes necessary to make hundreds of photographs, in rapid sequence, and in this case they will always be processed and printed on board.

While the problems of submarine periscope photography may vary slightly, depending on whether we employ an external camera attached to the periscope eyepiece, or whether we employ an internal camera incorporated in the periscope; it is believed that a discussion of the external camera will be of particular interest here. Just as would be the case if the camera were placed at the eyepiece of any telescope, the effective aperture ratio is determined by the ratio between the size of the exit pupil of the periscope and the focal length of the camera lens, also taking into consideration light

* Kollmorgen Optical Corporation, Northampton, Massachusetts. Presented at the PSA National Convention in New York, N. Y. 15 August 1952. Received 25 August 1952.



Fig. 2. Mosaic photograph made up of about 35 individual photographs taken with the MK 4 camera and processed.

losses due to reflection and absorption of light within the periscope. Thus, the effective aperture is fixed for any particular periscope and camera combination. We can only control our exposure through variations in shutter speed or through the use of appropriate light filters, choosing a film of a speed that will best suit existing light conditions. With the current still camera and periscope combinations, our widest effective aperture is about $f/14$, while our smallest effective aperture approaches $f/48$. Under poor light conditions, the small aperture poses an impossible problem, since time exposures cannot be made when photographing from a moving platform. However, under average conditions shutter speeds in the neighborhood of $1/50$ th or $1/100$ th of a second may be expected.

From the figures given above it is apparent that, for the most part, high speed films must be employed. Film

of speed group one hundred is usually satisfactory. Under adverse light conditions it is necessary to employ film of speed group two hundred, and we are looking forward to the day when there may be even higher speed films available. It is for this reason that color film has been little used in submarine still cameras although a considerable amount of reasonably good sixteen millimeter motion picture color film has been produced. This is possible due to the extremely short focal length of the motion picture camera lens. A few rolls of fairly satisfactory color film have been produced in the Mark 4 camera. This is possible only under conditions of brilliant tropical sunshine and through the use of a special, high speed, aerial type of color film. Shutter speeds of about one-tenth of a second were used, such long exposures being made possible by "panning" the periscope to counteract the image motion produced by the forward movement of the submarine.

To determine the correct exposure is not always easy. A photoelectric type of exposure meter cannot be used at the eyepiece of the periscope due to the small size of the exit pupil. However, if the opportunity presents itself, it is sometimes feasible to make readings with a photoelectric type of meter, on deck, while surfaced, and, thus, if light conditions do not change too rapidly, obtain a good basis for exposure when submerged. Of course, special highly-sensitive meters have been developed, but these are usually either too bulky or too delicate to permit their general use on a naval craft. A second method of obtaining exposure data is through the use of the American Standard Photographic Exposure Calculator. This device* takes into account all significant factors, including the type of target, whether the sun is overcast or clear, the month, the hour, and the latitude. In the hands of an experienced operator, the results are usually reliable. Similar data are also supplied to non-photographic personnel, in a simpler but less precise form, on an exposure data card which is calibrated for a particular camera and periscope combination, and which takes into account the altitude of the sun as well as atmospheric conditions.

Another problem which can be acute under submarine operating conditions is that of obtaining proper focus. The best visual focus is determined by individual characteristics of the observer's eye, and this is usually not

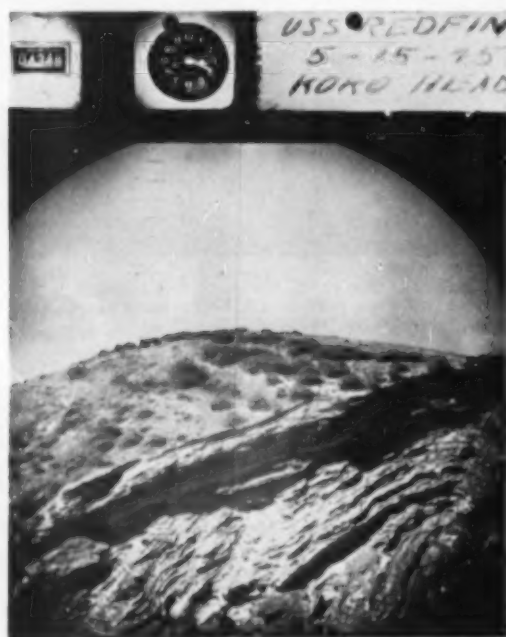
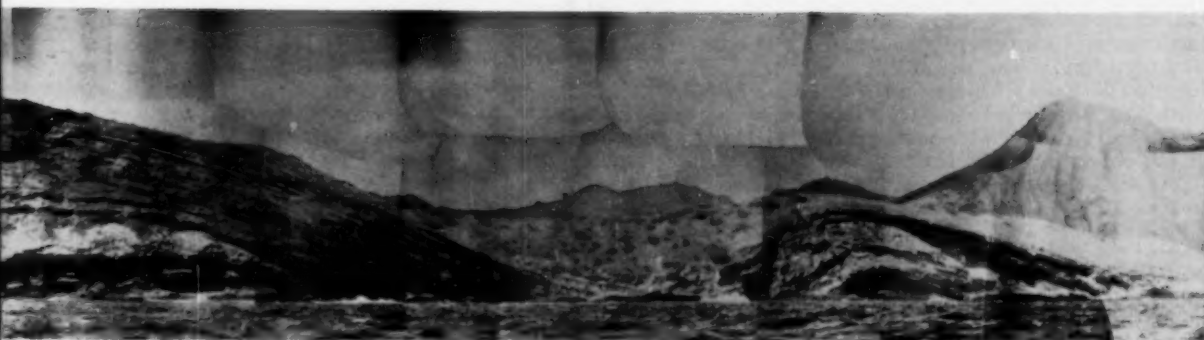


Fig. 3. One of a series of submarine reconnaissance photographs made by the USS Redfin during early tests of the MK 4 camera.

* See "Correct Exposure for Every Latitude," by J. W. McNair, *Photographic Science and Technique* Vol. 17B, No. 31, September 1951.



ard ship. Figure 3 below forms part of this typical reconnaissance photograph made through a submarine periscope.

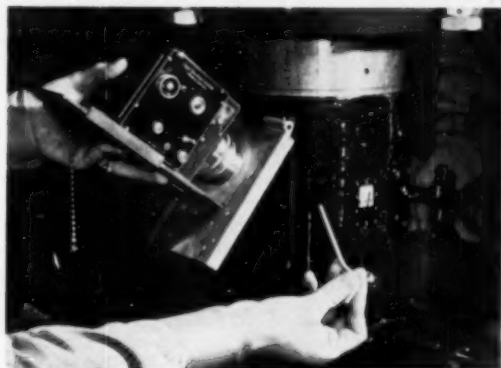


Fig. 4. Primarflex camera with special adapter being attached to periscope face plate for use in submarine reconnaissance photography.

the best photographic focus, which is at the zero diopter position of the eyepiece (the camera is focussed at infinity). The problem is complicated by the fact that the zero diopter position of the eyepiece may vary, from time to time, due to changes in the ambient temperature of the water or the air, or due to changes in the gas pressure within the hermetically sealed optical tube. At the outset, it was very difficult to make the operating forces understand this problem, and this lack of understanding was responsible for the loss of a great many valuable photographs. The solution to the problem is simple through the use of an auxiliary telescope or through the use of a ground glass placed at the focal plane of the camera. It is, of course, very simply solved where single lens reflex cameras can be employed. However, these cameras are not always convenient since they cannot be used at eyelevel, the normal position of the periscope eyepiece; and, since they are more bulky, heavier, and represent considerable mechanical complexity. Therefore, they pose a more serious maintenance problem than a simpler form of camera. There is the added disadvantage that non-photographic personnel are often confused by the reverse image appearing in the ground glass.

An important secondary problem concerns the use of colored ray filters. Due to the small effective apertures, it is frequently undesirable and sometimes impossible

to employ a filter of any kind. However, there are certain advantages to the use of a filter where light conditions permit. Yellow or minus-blue filters are helpful under hazy conditions and, also, they will increase the contrast of the image which may be low due to the long complex optical path of certain types of periscopes. A filter may also serve to reduce the effect of longitudinal color aberrations, which are to some extent, present in every telescopic or periscopic eyepiece.

A number of different types of both still and motion picture cameras have been used on periscopes. The first camera to appear in the submarine fleet was the Kodak Medalist. While this may be an excellent camera for ordinary purposes, it is entirely unsuited for submarine photography since it is impossible to see the image through the single eyepiece and photograph it at the same time, or even at nearly the same time. The first cameras to be supplied the submarine fleet in quantity were known as the Mark 1 still camera and the Mark 2 motion picture camera. The Mark 1 camera was a standard Kodak 35 provided with an attachment for adapting the camera to the periscope eyepiece and

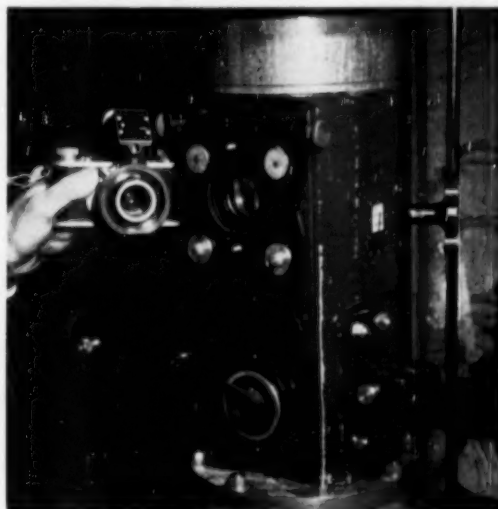


Fig. 5. A 35mm MK 1 submarine periscope camera about to be placed at the eye piece of a periscope.

with a light-splitting block in front of the lens to permit simultaneous viewing and photography. Due to its short focal length lens, the effective aperture is greater than that obtained with most other still cameras. It is difficult to obtain good focus with this camera and, due to the small film size, large photographs of good quality are not obtainable. The Mark 2 camera is a modification of a standard Kodak, magazine load, sixteen millimeter motion picture camera. This camera is also provided with an attachment for mounting it at the eyepiece of the periscope, and with a splitting element in front of the lens to provide simultaneous viewing and photography. The proper focus is fairly convenient to obtain through the use of a boresighting and focusing device which is provided as an accessory to the camera. Of course, the same focus setting can also be used for the Mark 1 camera.

During the early phases of World War II, a number of different types of single lens reflex cameras were used for reconnaissance purposes. Typical of these cameras was the Primarflex camera, which used 120 size roll film and had an eighty millimeter lens. This camera had the ability to produce good negatives of a reasonable size, and allowed the photographer to observe the image up until the instant the photograph was taken. Fine focus was easily obtained with the ground glass viewing screen. However, this camera, as well as others of the same type, did not stand up well under wartime patrol conditions and it was usually necessary to take two or three cameras on each patrol and, even then, the photographer usually had to repair the cameras several times during the course of the patrol.

In 1944 the U. S. Navy undertook the design of a camera to be used for reconnaissance purposes which is known as the Mark 4 camera. The Mark 4 camera is of the single lens, reflex type, having a detachable magazine containing about one hundred exposures on $5\frac{1}{4}$ " aerial roll film, and having a five inch lens. Data consisting of the time of day, the exposure number, and a data card are automatically recorded on the film along with each exposure. This camera has produced reconnaissance photographs of outstanding merit, but, due to its size and weight, is not convenient to use for record purposes.

During reconnaissance missions it is usually necessary to process and print while at sea all exposed film. Due to the meager amount of space that can be made available, and due to certain abnormal photographic conditions, this can be a severe problem even though it is basically a simple photographic process. An example of this is one wartime patrol made by the writer into

tropical waters during which, in one two-week period, over two hundred rolls of size 120 film were processed in the officers shower bath. This space is about five feet long and less than three feet wide. When it was sealed to make it light-tight, the temperature rose to over 100 degrees F. with the relative humidity over ninety percent. Naturally, it was necessary to use special hardening baths, but, even so, the emulsion was soft and easily damaged, and it was impossible to completely avoid reticulation. The film base became so limp the film could not be loaded into the regular roll film processing tanks. A great many rolls of film were run through the tanks by hand, until the establishment of a procedure of splicing rolls together and developing them in an aerial roll film developing tank.

During this same two-week period, two prints were made of each negative and one set of prints was mosaiced into strips of eight to sixteen prints each, for preliminary photographic interpretation purposes. It is of interest to note that in the case of a coastline held by the Japanese, a number of gun emplacements were spotted, using stereo pairs of photographs, which had not been observed during two prior visual examinations of the coastline.

Generally speaking, film is developed in submarines in a normal manner with normal commercial developers. However, the development is frequently forced, to a certain extent, in order to provide an increase in contrast to make up for the contrast that is lost as the image passes through the long chain of optics in the periscope. Some use has been made of special film and special rapid processing procedures in order to produce a negative for viewing purposes in the shortest possible time. Rapid processing film holders were designed for both the Mark 1 and Mark 4 cameras to allow single exposures to be made and processed immediately, with the film still in the holders, in order to allow the skipper to check his observations in a more leisurely manner. This is desirable since, for obvious reasons, during an attack, the periscope is exposed above the water for the briefest possible period of time. Using the rapid processing technique, it has been possible to obtain negatives for viewing purposes within about sixty seconds after the exposure was made.

It is concluded that the technique of submarine periscope photography has advanced at a rather rapid rate and has been of considerable military value. There seems little doubt that periscope photography is here to stay despite severe limitations in space and personnel, and despite the very poor photographic conditions that naturally exist on board a submarine.

ON THE MECHANISM OF PHOTOGRAPHIC SENSITIVITY IN SILVER BROMIDE*

It has been shown recently by Loening¹ that pure silver bromide in the form of an aqueous sol has only a very slight sensitivity to light as judged after development. Sensitization can be achieved by adding silver ions or gelatine or substances such as sodium nitrite to the sol. Ordinary photographic emulsions have already the sensitivity con-

ferred by gelatine and there are three well-established methods² of obtaining further gains of sensitivity, depending on the addition of (i) reducing agents, (ii) gold salts, and (iii) sulphur compounds. These substances probably react with the silver bromide to form minute quantities of silver, gold, and silver sulphide respectively at the grain surfaces: at any rate that is the simplest supposition. All this refers to "chemical" sensitization, as distinct from extension of spectral sensitivity by dyes.

According to the theory of the photolysis of silver bromide pur-

* Communicated by G. L. P. Levenson on behalf of the Scientific and Technical Group of the Royal Photographic Society of Great Britain. Received 5 December 1952.

forward in 1938 by Gurney and Mott³ the absorption of a light quantum by silver bromide removes an electron from a bromide ion, leaving a "positive hole." The electron and the hole should both be highly mobile. If silver particles are present they become negatively charged by trapping electrons and grow by attracting the mobile interstitial silver ions that are naturally present in the crystal (Frenkel disorder). This theory still holds the field. More recent attempts based on the assumption of Schottky disorder have now been abandoned.⁴ As applied to latent image formation, however, the theory is incomplete: one has to explain how the first electrons are trapped if no silver is initially present. What is lacking is evidently a theory of sensitization, and the question arises: do the sensitizers mentioned above function as electron traps, or positive hole traps, or both?

In a lecture before the Scientific and Technical Group of the Royal Photographic Society 20 November 1952, Dr. J. W. Mitchell described a series of elegant experiments on the point carried out by himself and collaborators at Bristol University. The complications of photographic emulsion work were avoided by using pure dry monocrystalline plates of silver bromide and applying the sensitizer (silver, gold or a metallic sulphide) directly in a very thin uniform surface layer by vacuum evaporation. The plates were about 1 cm square and 0.01 cm thick with the crystallographic [100] axis approximately perpendicular to the square face. An ordinary MQ developer was used with a little gelatine added to prevent excessive fog. Unexposed unsensitized specimens gave only a slight irreducible fog in the form of small oriented silver crystals scattered over the surface, as observed in previous single-crystal work by Dankov⁵ and Boissonnas.⁶ Exposure to light produced no further developable effect, even when sufficient to produce visible (internal) separation of silver. A developable latent image was produced, however, by exposure under a solution containing a bromine acceptor.

By means of slits and masks the deposition of sensitizing substances and the exposure to light were restricted to well-defined circular or rectangular areas of the specimen. Areas bearing 10^{18} silver atoms per cm^2 (about one monolayer) were blackened by development without exposure, the edges appearing well defined. Specimens bearing 10^{14} silver atoms per cm^2 gave only the normal irreducible fog without exposure, but were blackened in certain areas by development after exposure, i. e. were sensitized but not fogged by the deposited silver. This blackening or latent-image formation was expected to occur only in the areas both silvered and exposed to light, but the result was quite different. The blackening appeared only in the unexposed areas, and spread beyond the silver areas, the spreading being greater at a greater distance from the exposed area: with sufficient exposure the entire unexposed area became blackened. Essentially the same phenomena

were observed with gold and with arsenious, antimony and thallous sulphides (silver sulphide, not being stable enough for evaporation, was not tried).

If the sensitizers in these experiments acted mainly as electron traps the blackening would presumably have been confined to the sensitized areas. It seems that the phenomena can only be explained by supposing that they act as positive hole traps, i. e. react with the bromine, which is quite reasonable from a chemical point of view. If some of the bromine is removed in this way, a surplus of electrons remains, and apparently no special electron traps are then needed to ensure the formation of latent-image silver specks, for the latent image appears largely on the naked silver bromide surface. The mobility of the electron being about twice that of the positive hole explains why the image is produced far from the exposed area, in which a surplus of positive holes will be left. The space charge produced by the electrons travelling faster than the holes would produce a field urging interstitial silver ions into the electron-rich regions. Dr. Mitchell did not, however, attempt to give a complete theory of the phenomena.

It appears then that (i) silver, gold, and metallic sulphides all sensitize by the same mechanism, (ii) the function of each is to react with halogen, and (iii) no special electron traps are needed for sensitivity. In the case of silver sensitization, the capture of positive holes by the silver permits the formation of new silver elsewhere by the electrons and interstitial ions, and one might say that in effect the latent image is formed by redistributing the silver initially present. These tentative conclusions, though they may not be directly applicable to the sensitization of ordinary emulsions, are of obvious interest to the photographic chemist and represent a radical revision of earlier thought on the subject.

References

1. E. E. Loening, *Fundamental Mechanisms of Photographic Sensitivity*, ed. Mitchell, (Butterworths Scientific Publications, London, 1951), p. 149; *Phot. J.* Vol. 92B, p. 126 (1952).
2. W. G. Lowe, J. E. Jones and H. E. Roberts, *Fundamental Mechanisms*, p. 112.
3. R. W. Gurney and N. F. Mott, *Proc. Roy. Soc.* Vol. A164, p. 151 (1938).
4. J. W. Mitchell, *Sci. Ind. Phot.* Vol. 19, p. 361 (1948); *Phil. Mag.* Vol. 40, p. 249, 667 (1949).
5. P. D. Dankov and A. A. Kochetkov, *Compt. rend. Acad. Sci., U. S. S. R.*, Vol. 26, p. 785 (1946).
6. C. G. Boissonnas, *Sci. Ind. Phot.* Vol. 20, p. 361 (1949); *Experientia*, Vol. 5, p. 282 (1949); *Fundamental Mechanisms*, p. 36.

MODIFICATION OF LACQUERS FOR PROTECTIVE COATING OF PHOTOGRAPHS

Hubert O. Ranger*

ABSTRACT

Developments in lacquer technology since most photographic lacquers now on the market were formulated, suggested the need for re-examination of these lacquers in the light of the needs of present-day photographic materials.

A number of promising new components were chosen and examined. Some were found useful in supplementing or replacing present lacquer constituents. Vinylite VYCC contributes greatly towards providing a superior lacquer, and the addition of ultra-violet absorbers is helpful for preserving color photographs.

OBSERVATION that many new resins have appeared since the advent of most photographic lacquers now available, prompted this work. It is appreciated that lacquering is an additional step and expense in finishing a photograph, but after it is seen that a real contribution is made by lacquer coating, its use is justified.

With the premise that any photograph made with trouble and expense, such as most color photographs, is worth preserving indefinitely the contribution of a good protective lacquer can be appreciated. In recent years the only emphasis on protective lacquers seems to have been given by cinematographers while the still photographers have viewed lacquering as an added luxury to be used only by perfectionists. The main objective in motion picture work¹ has been providing protection for the emulsion and base from abrasions and providing a

* The Plastic Coating Corporation, Holyoke, Massachusetts. Presented at the PSA National Convention in New York, New York, 16 August 1952. Received 11 August 1952.

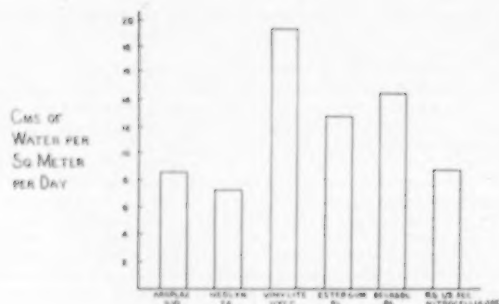


Figure 1: The moisture vapor transmission rates of the resins tested.

lubricating layer for easier and quieter passage through motion picture equipment. The study reported here expands the components of protective lacquers to more completely encompass the innate weaknesses of photographic prints and transparencies, particularly color materials.

It is widely appreciated that heat, light, high humidity, grease and oil, and physical abuse acting separately or especially in combination greatly decrease the life expectancy of a photograph. If a coating were applied which eliminates or minimizes these outside influences extended usage of, for example, color prints would be more feasible for such things as window displays, outdoor advertising, continual audio-visual presentations, or photographs for the home collection which may meet the adverse conditions of a hot attic, damp basement, or almost daily exposure to sunlight.

Towards this end an examination of the technical literature of recent vintage on lacquer components providing protection from the above mentioned adverse affects was made and several promising components were chosen for detailed examination.

This is by no means an exhaustive study since the volume of literature and interesting new components available is unbelievably large. This admittedly limited study, however, led to some interesting results. A number of commercially available lacquers were tested first to determine which weaknesses should be overcome to make a lacquer providing the protection required. The outstanding weaknesses found were high water vapor transmission rates and high ultra-violet radiation transmission. This is not particularly surprising when it is realized that the expressed purpose of most lacquers is protection from physical abrasions, but coating resins are available which provide superior protection even in this respect.

Photographic prints were aged under various adverse conditions and the results observed. This led to the conclusion that a lacquer providing the following was needed: (1) low WVTR (water vapor transmission rate), (2) filtering action to most of the rays in the ultra-violet region, (3) high abrasion resistance, (4) non-yellowing under ultra-violet radiation, (5) resistant to the penetration of grease and oil. A primary consideration is that the lacquer must adhere to the photographic coating since it is obviously of little value if it does not. With regard to the first characteristic it is important to distinguish between moisture and mois-

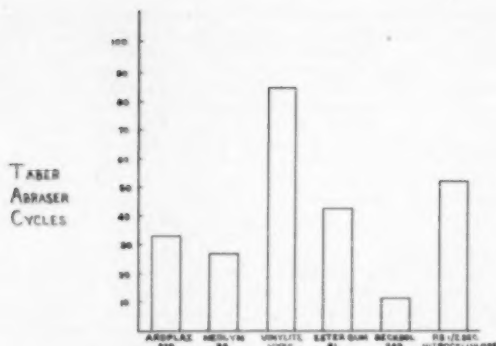


Figure 2: The relative resistance to abrasion of the resins tested. The compositions tested were 10% resin, 60% plasticizer, and 30% nitrocellulose.

ture vapor transmission. A coating may be very water resistant and yet readily transmit water vapor. Either will adversely affect a photograph.

It is not necessary to be a lacquer technologist to appreciate the fact that it would be nothing short of a miracle if all these properties were provided by one substance. It also should be realized almost any lacquer is a mixture of compromises which gives some of the desired results at the expense of part of other desired results.

The conclusion after examining the literature was to limit the examination to six film formers, one or a mixture of which would be the foundation of a new lacquer. The resins examined* were Aroplaz 930, Neolyn 24,

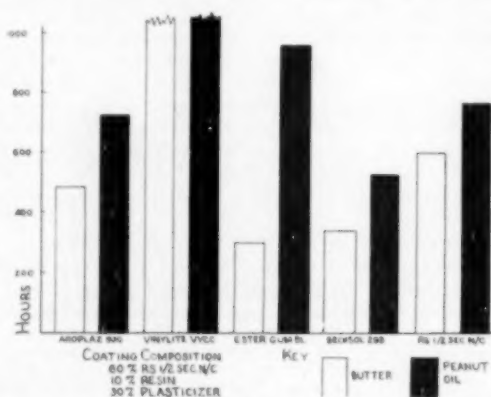


Figure 3: The relative grease and oil resistance of coatings from the resins tested.

Vinylite VYCC, Ester Gun 8L, Becksol 29B, and 1/3 sec. RS nitrocellulose. The latter substance is provided as a control since it is the main film former in most commercial lacquers. Neolyn 24 was included not because it would be usable by itself but because it has characteristics which make it of interest for blending with

* Sources for the resins are as follows: Aroplaz 930, U.S. Industrial Chemicals, Inc.; Neolyn 24, Hercules Powder Co.; Vinylite VYCC, the Bakelite Division of Union Carbide and Carbon Corp.; Ester Gun 8L, Hercules Powder Co.; Becksol 29B, Reichhold Chemicals, Inc.

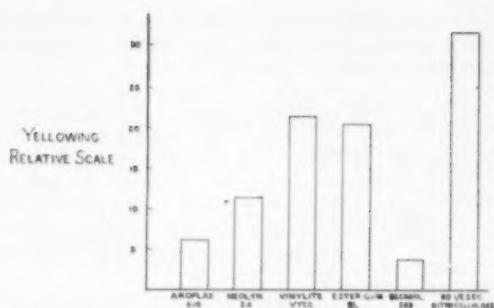


Figure 4: Relative yellowing of the resins tested. Dried films of each resin were exposed to an ultra-violet source for equal times.

something else. Its color limits its usefulness by itself for photographic purposes. The choice of a film former as a starting point is very desirable in lacquer formulation because it limits the field of plasticizers, solvent, and waxes due to compatibility considerations.

A commercial uncoated photographic paper base was adopted for all comparative physical tests on the various coatings and equal amounts of lacquer coating were used in all cases. The WVTR test was made according to The TAPPI¹¹ standard and the results are shown in bar graph form in Figure 1. These results indicate that something is still desired in this respect. A wax usually helps minimize WVTR, but the choice of a suitable wax was postponed until the film former was decided upon. This is discussed later in the paper.

Abrasion resistance was examined next, using The Taber Abraser with the results obtained illustrated in Figure 2. It is seen that Vinylite VYCC is much superior to the other resins in this respect.

Grease and oil resistance was tested by using a glass cylinder with grease and oil resistant cement fastening it to the paper coated with the lacquer in question. The grease and oil used for testing were poured into the cylinder with the paper placed on a glass shelf. The bottoms of the sheets were observed at regular intervals until penetration was apparent. The results are shown in Figure 3.

At this point Vinylite VYCC appears to be a very desirable coating material. However, Figure 4 shows the results of yellowing resistance tests, made by exposure to ultra-violet, in which Vinylite VYCC falls down. Because this resin is so desirable otherwise, it was felt that further examination for prevention of its yellowing was warranted. Chemically the resin is a vinyl chloride-vinyl acetate copolymer in which 62% is vinyl chloride. Light decomposition of such substances is a familiar phenomenon and literature on stabilizers for them is voluminous.^{4,7,10}

These stabilizers can be divided into three general classifications; (1) ultraviolet absorbers, (2) hydrogen chloride acceptors, and (3) substances which will combine with a conjugated double bond system which has lost hydrogen chloride. Since it is desired that our photographs also be screened from ultra-violet radiation the use of such an agent can serve a double purpose. This effect can be achieved without addition of undesirable color by the use of such compounds as the benzo-

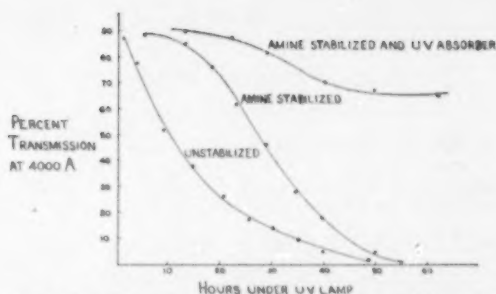


Figure 5: The results of stabilization of Vinylite VYCC against the effects of ultra-violet radiation.

phenones. The dihydroxy compounds are especially good and of these isomers the 2,2' compound appears to be the best ultra-violet absorber.¹

Since the ultra-violet absorber is mixed intimately with the resin it is obvious that the resin near the surface will not be screened as completely as the resin on the bottom. The results of the partial stabilization obtainable is illustrated in Figure 5. For the remaining stabilization necessary a weak hydrogen chloride acceptor, triethanolamine,⁸ was examined. The effect of varying amounts is shown in Figure 6. It might seem from this illustration that the more triethanolamine present, the better the stabilization.⁹ The fact is, however, that too much hydrogen chloride acceptor causes the release of hydrogen chloride to a greater extent than ultra-violet light. A good compromise seems to be about 20% of the theoretical amount needed to accept all the hydrogen chloride releasable by the resin. The results of combining chemical stabilization with ultra-violet screening is shown in Figure 5.

A further complication in the use of an ultra-violet absorber was observed. Such substances appear to be anisotropic which means that the amount of absorption of the ultra-violet they provide depends on the angle at which the light strikes the protective layer. For the purposes of this study that phenomenon was overlooked since it does not seem to be extreme enough to interfere seriously.

The foregoing provides an effective coating layer in the form of Vinylite VYCC plus a stabilizer which shields the photograph from deteriorating radiation. The coating must now be plasticized. An examination of the literature on plasticizing vinyl resins resulted in several possibilities. They were tricresyl phosphate, dibutyl sebacate, Santicizer B-16 (butyl phthalyl butyl glycolate),* and Flexol 3GO (triethylene glycol di-2-ethyl hexoate). These were tested in equal amounts for gloss, blocking resistance, and flexibility. Blocking was tested by stacking sample coatings face to back under weights which provided 1 lb./sq. inch in an oven at 120F. The results were examined after twenty-four hours. Flexibility was observed by folding samples in either direction and noting the tendency to crack. The best compromise among the plasticizers appeared to be tricresyl phosphate. Quantitative data for this choice are difficult to obtain except for gloss and since this is one of the minor requirements no data are presented.

* Santicizer B-16 is a product of The Monsanto Chemical Co. Flexol 3GO is a product of The Carbide and Carbon Chemical Co.

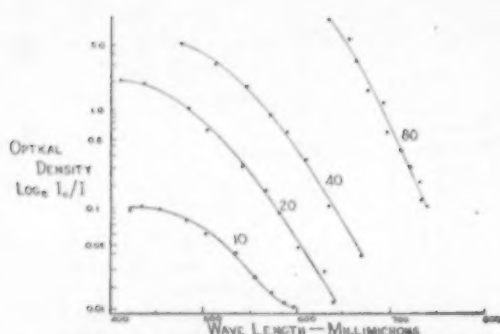


Figure 6: The results of stabilization of Vinylite VYCC with various amounts of triethanolamine against the effects of ultra-violet radiation.

A very interesting plasticizer, which might be of value as a substance which plasticizes and absorbs ultra-violet radiation at the same time, is *o*-nitrobiphenyl, but it was not included here because it was considered too volatile for a long-life plasticizer.

The need for more water vapor resistance was mentioned earlier. This is provided by the addition of a small amount of wax. Several waxes were examined and the most suitable was a microcrystalline wax. The results of the addition of increasing amounts of wax plotted against WVTR is shown in Figure 7.

In designing a solvent system, the principles used in general lacquer formulation apply to photographic lacquers as well. A high boiling solvent such as butyl acetate is necessary to prevent blushing and its amount must be varied depending on the method of application to be utilized. A small amount of medium boiler is needed to provide an even rate of drying, and low boilers are provided in sufficient quantity to allow drying as rapidly as possible without bad effects from flow marks. The balance of the solvent composition is thinner, or diluent, which should be a low-cost volatile liquid that can be tolerated by the other substances present. Such a substance is toluol.

By putting all the components together a complete lacquer is obtained which needs only minor adjustment

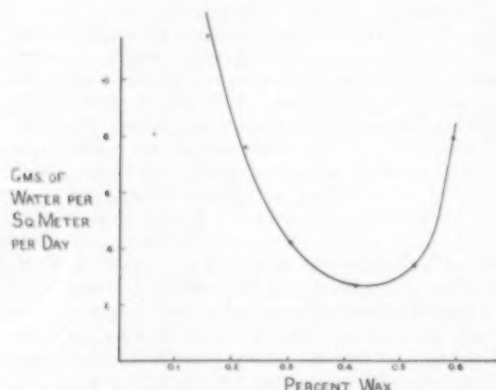


Figure 7: The effect of microcrystalline wax in a lacquer on moisture vapor transmission rate.

to make it suitable for different photographic materials. The formulation which follows is a typical one balanced for spraying onto paper prints.

1/2 Sec. RS nitrocellulose	1
Vinylite VYCC (40% in BuAc)	6.3
Tricresyl phosphate	2
Butyl acetate	6
Butanol	1
Ethyl acetate	1
Ethanol	1
Toluol	15
Triethanolamine	1.6
2, 2'-dihydroxybenzophenone	0.1
Microcrystalline wax	0.3

The nitrocellulose is present in this formulation for adhesion purposes. Without it the film can be stripped from the paper after it dries. It is possible to obtain good adhesion without the nitrocellulose if a two-coat system is used. The first coat should be a melamine resin acid colloid and is applied from a water solution and dried. This forms an anchor coat to which the vinylite VYCC will bond firmly.

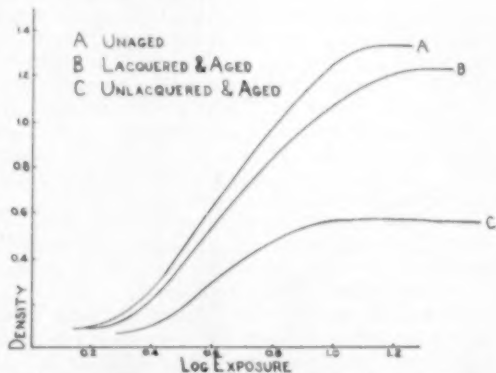


Figure 8: The cyan layer sensitometric curve of color print step wedges showing the effects of aging with and without lacquer coating.

Color prints were lacquered with the above composition and aged under adverse conditions. The aging was carried out until the unlacquered print appeared too deteriorated to be of any value. Sensitometric curves were prepared before and after aging on lacquered and unlacquered step wedges. The cyan curve is shown in Figure 8. From that set of curves it can be seen that, while some loss in gamma and maximum density occurred in the lacquered sample, it does not approach the loss which occurred in the unlacquered sample.

Many interesting variations have been made with lacquer formulations such as the one given here. One of the different things done was to add flattening agents to the lacquer to allow the lacquering of a matte print without gaining undesirable gloss. Varying amounts of flattening agents can be used to obtain any degree of gloss desired. Another variation was the addition of small amounts of opaquing agents for use as a retouching lacquer. With this lacquer only the part which is desired as subordinate subject matter is lacquered. The contrast to this area is decreased while the unlacquered

portion retains its contrast. This area can then be covered with clear lacquer. A further variation is the addition of dyes to lacquers to simulate toning or to provide color correction for transparencies slightly out of color balance. This, of course, requires some practice.

From the foregoing information it can be seen that the use of a suitable lacquer can make an appreciable contribution towards preserving photographs, and, although lacquering means additional work and expense in finishing operations, that step is paid for in the gain of life expectancy for the photograph.

References

1. Boyer, R. F., Matheson, L. A., and Moyle, C. L., U. S. Patent 2,264,291 (1942).

2. Chapman, A. F., U. S. Patent 2,533,557 (1950).
3. Charch, W. H. and Bateman, D. E., U. S. Patent 2,159,009 (1939).
4. Hendricks, J. G., White, E. L., Ind. Eng. Chem., Vol. 43, No. 10, pp. 2356 (1951).
5. Matheson, L. A. and Boyer, R. F., Ind. Eng. Chem., Vol. 44, No. 4, pp. 867 (1952).
6. "Preserving 8mm and 16mm Film," pamphlet by the U. S. Photographic Equipment Corp.
7. Marvel, C. S., Horning, E. C., and Gilman, E., "Organic Chemistry, An Advanced Treatise," Vol 1, 2nd ed., p. 274, John Wiley & Sons, New York (1943).
8. Wiley, R. M., Alquist, A. G., and Slagh, H. R., U. S. Patent 2,160,949 (1939).
9. Wiley, R. M. and Livak, J. E., U. S. Patent 2,933, (1941).
10. Wilson, J. E., J. Am. Chem. Soc., Vol. 72, pp. 2905 (1950).
11. TAPPI Standard Code No. T448 M-49, Official Oct. 1941; Revised Aug. 1944. Technical Association of the Pulp and Paper Industries.

MOTION PICTURE AND FLASH PHOTOGRAPHY IN MECHANICS RESEARCH

Clifford C. Hauver*

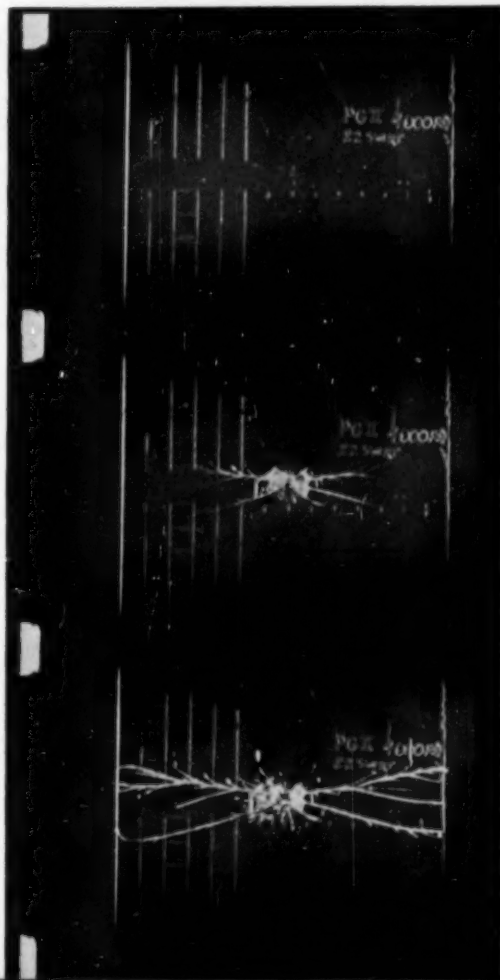
DURING recent years the role of photography in scientific research has been one of growing importance. Among the factors contributing to this growth are new flash illuminating techniques, higher speed film emulsions, and rotating prism type motion picture cameras. This paper reviews briefly some of the methods which are now being employed in mechanics research.

Certain investigators at the Naval Research Laboratory are for the most part concerned with pulse jet engines, penetration and damage ballistics, fracturing of metals and plastics, and various subjects in the field of shock and vibration. The events for which photographic records are required are sometimes self luminous, for example, impact flash, deflections of the focal spot on an oscillograph screen, and a variety of instrumentation using streak photography. Frequently, however, high-speed motion picture and flash photography of non-self-luminous subjects is required. They present special problems. Examples of events for which fast pictures are required are the fracturing of metal bars, cracking and shattering of stressed metals and plastics under impulsive loads, ballistic penetration of metals and plastic, impact flash studies, and reaction of complex instruments to mechanical shock.

At the present time high speed motion pictures are being made in the 3000 to 15,000 pictures per second range, and are obtained by using standard commercial equipment designed for this use. Lighting, however, presents a difficult problem. There are two main causes, the subjects in most cases are sensitive to heat and quite often cover relatively large areas. In most cases the use of 750R reflector floods or spots is impossible because of their intense heat.

Currently Fastax lamps have been used with satis-

Fig. 1. Enlarged frames from 16mm high-speed film showing shatter of a transparent plastic plate that has been struck by a cal.22 bullet.



* Navy Department, Naval Research Laboratory, Washington 25, D. C. Presented at the PSA National Convention, New York, N. Y., 13 August 1952 as part of the Technical Division Symposium on Photography in Engineering and Science. Received 4 October 1952.

factory results for areas not over six inches square. These lamps use a 750-watt projection lamp which can be focused by a movable reflector for maximum brightness. They also contain a water cell which greatly reduces the heat output.

For the illumination of larger areas than can be lighted with incandescent type lamps, a Lester Continuous Flash Lighting Unit is employed. The desirable features of this type of lighting are its high intensity, coolness as compared with incandescent type lamps, and lack of special heavy wiring so often needed when several incandescent type lights are used.

A 16mm Eastman Type III camera as well as an 8mm

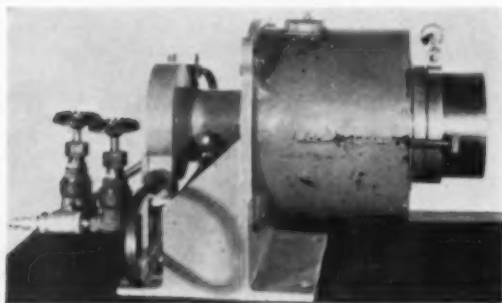


Fig. 2. General view of drum type camera under construction at the Naval Research Laboratory.

Fastax camera, operating at 15,000 frames per second are used. The Eastman camera is started before the Fastax camera as it requires more time to come up to speed and runs for somewhat longer than one second, whereas the film in the Fastax camera is exposed in about 0.8 second. One hundred-foot rolls of film are used. Figure 1 shows three enlarged frames of the record obtained by the 16mm Eastman Type III camera operating at 3000 frames per second. The Cal. 22 pellet is just striking a sheet of transparent plastic. Only one picture was obtained before the cracks reached the edge of the sheet. Although more frames of this important stage of the event could be obtained with the 15,000



Fig. 3. 10 unit FT/25 type flash lamp used for pulsed light exposures with the NRL drum type camera shown in Figure 2.



Fig. 4. High-speed still photograph of a steel cylinder emerging from cloth laminate armor material. Taken by the Edgerton equipment and triggered by the emerging missile.

frame per second Fastax record and these permitted useful measurements, the clarity possible with 8mm film leaves much to be desired.

Picture frequencies as high as 15,000 per seconds often do not provide time enough so that scientific records can be obtained for detailed study. The laboratory is now in the process of constructing a drum type camera. (Figure 2). With this camera it is hoped to obtain ten pictures on 35mm film at a frequency of about 30,000 per second. The camera is of the single prism type and the prism is rotated by an air turbine. A pulsed light source is required.

The unit shown in Figure 3 has been constructed, using ten electronic flash lamps of the FT125 type. Each lamp has its own power supply with a built-in delay circuit from 0 to 200 milliseconds. The duration of each flash is in the 1 to 2 microsecond range.

For still pictures requiring exposure times less than 1/1000 second the Edgerton type equipment is used.

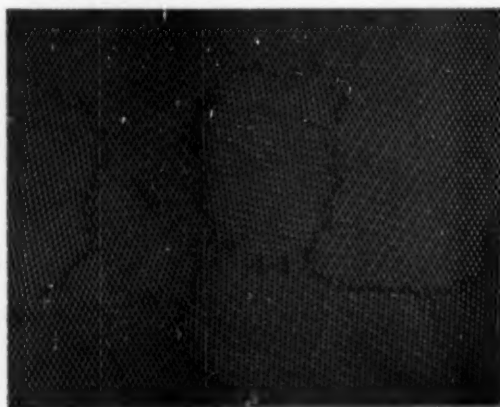


Fig. 5. High-speed still photograph of a bubble model during deformation. This model simulates the movement of lattice dislocations which accompany deformation of a ductile polycrystalline metal.

In most cases the work is done in a darkened room using the open shutter technique. After the camera is focused, the shutter is set on time, the lights are turned off and the shutter is opened. The motion of the object to be photographed causes interruption of a narrow light beam focused on a photocell. The electric signal from this event triggers a strob light. If it is desirable to use sound waves to trigger the light source, the photocell is replaced by a microphone.

An example showing use of this method is shown in Figure 4. Here the object of the photography is to record the bulging and tearing of a cloth laminate armor plate at the moment a simulated missile has just completed penetration. In the figure the conical end of the steel cylinder is shown emerging from the spray of cloth fragments.

Figure 5 shows a flash picture of an array of uniform size bubbles at the surface of a glycerine-aerosol-water mixture. Bubble arrays of this kind are used to model dislocations in ductile crystalline solids. The dislocations, or regions of lattice imperfection, shown in this model, were moving rapidly as the bubble raft was steadily distorted in such a way as to produce general features similar to a polycrystalline metal during deformation.

During its first stages of development a crack such as that shown in Figure 5 moves so slowly that time lapse pictures at five-second intervals are necessary to study its progress. After the crack develops into unstable rapid motion, 15,000 frames per second pictures are scarcely fast enough for the study of limiting velocities attained and for observing the appearance of the fast fracture. Thus single events requiring a change of the photographic observation time interval by a factor of 100,000 sometimes occur in mechanics research. By

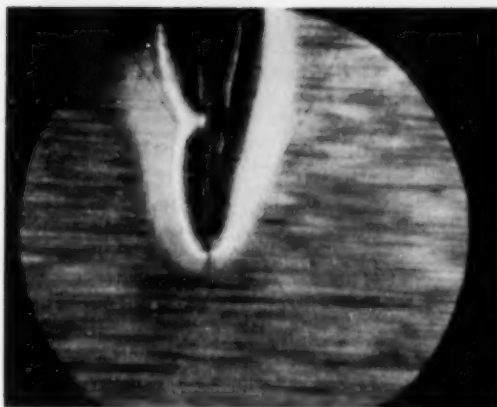


Fig. 6. Photomicrograph made by use of Strob light showing crack in aluminum foil. The crack and foil were in gradual motion as the foil was being pulled in tension.

the drum camera method, discussed above, it is hoped to attain desired faster frame speeds and larger pictures. This method, however, will permit only ten exposures and is costly with respect to light source instrumentation. For fast motion picture and flash photography of non-self-luminous subjects, photographic tools now available are an indispensable aid to many mechanics investigations as illustrated above. New as they are, the limitations of these photographic tools are already keenly felt. There is a challenging and growing need for higher camera speeds and more intense short-duration lights.

HIGH-SPEED PHOTOGRAPHY IN MEDICINE

John H. Waddell*

ABSTRACT

High-speed motion picture applications to the study of various organs are described. The techniques and results obtained from high-speed photographs of the larynx, eardrum, heart, and muscular motion are discussed.

HIGH-SPEED PHOTOGRAPHY as applied to medical and anatomical studies is a relatively new technique. The new knowledge obtained by slowing down motion so that the eye and the mind can observe the action is such that text books are being re-written. A review of experiments reveals interesting progress.

In 1936 the high-speed motion picture camera was used by the Bell Telephone Laboratories to study the vocal cords. There had been some earlier attempts, or trials which were made simultaneously, by other organizations. The pictures obtained at Bell Laboratories,

however, were unique in that the action of the cords during phonation was made visible for the first time.

A 16mm high-speed camera was used to take 4000 pictures per second of male subjects saying, "Aw" at a pitch of 125 cycles per second. Approximately 2 seconds were required to view 1 cycle when these pictures were projected at 16 pictures per second. Furthermore, still pictures were made from the sequence pictures for measurement purposes. In the first work done at the Bell Telephone Laboratories the subjects were not anesthetized. Only male subjects were successfully photographed, because female subjects were not able to coordinate all of the required actions and still not gag when the required throat mirror was placed in the back of the mouth.

In the photography of the vocal cords the primary

* Wollensak Optical Co., Rochester, New York. Presented at the PSA National Convention, New York, N. Y., 12 August 1952 as part of the Technical Division Symposium on Photography in Medicine and Biology. Received 22 November 1952.

problem was that of lighting. Normally in the medical photography of cavities one uses a flat light, such as is obtained with a ring light or photoflood types. The ideal way of getting light down a hole is to use the same optical path that the lens has. Therefore, the image of a filament from a projection lamp was focused through an aspheric condenser to a plane mirror, which was at 45° to the optical path of the lens. The light then was reflected from this mirror to a throat mirror and the image of the filament was brought into focus at the plane of the cords. There was only one disadvantage at this stage. The image of the filament got extremely hot thus introducing the danger of burning the oral tissues. Therefore, a water cell was placed between the condenser lens and the plane mirror. This water cell was approximately 6 inches thick. (Further experiments have later shown that such a thickness is not needed.) The plane mirror was of the second-surface type and an elliptical hole was made on the silver surface so that the lens could be directed through the clear glass. It can be pointed out that a partial reflection-transmission mirror can be used for this purpose, although about $\frac{2}{3}$ of the light is lost in this way. Aklo heat-absorbing glass has since been used, but with imaged filaments this glass has a tendency to crack.

A large number of studies of the cords were made. These surveyed the voicing of various tones at different intensities, the effect of using helium gas to make the voice similar to that of a eunuch, the effect of breathing, the start of phonation, coughing, sneezing, and phonation under pressure. The summary of these films is contained in two releases which are available from the Bureau of Publication, Bell Telephone Laboratories in New York.

A whole new realm of vocal-cord photography is now ahead of us, with the 16mm camera, which was used in these experiments, now being "souped-up" to take 8000 pictures per second. Furthermore, under a local anesthetic, the maximum frequency of the voice of both males and females can be observed and analyzed.

As an offshot to these experiments the equipment for taking vocal cord pictures was shown in "mock-up" to Dr. Barney M. Kully of Los Angeles at the Bell Telephone Laboratories in 1948, for modification. He had Mr. Arthur Neihart build the first Intraflex



Fig. 1. Successive frames of a 16mm high-speed motion picture showing action of the human vocal cords in phonation.

30



Fig. 2. The motions of the heart become apparent as it is approached through the pericardium. In this 16mm high-speed motion picture made on color film, the tip of the left auricular appendage is seen through the opening.

Camera for taking 16mm motion pictures of cavities. There is currently under development a set-up which can be adapted to utilize any type of camera for taking pictures of details in cavities. It is comparatively simple and could easily be used in hospitals without any danger of explosion. It is based on the original Bell Telephone Laboratories technique.

These studies of the vocal cords were conducted under the direction of Dr. J. C. Steinberg. The result is a complete new concept of the behavior of the vocal cords in the formation of speech. These findings are now recorded in the literature and many of the former premises have been discarded.

Eardrum Rupture Studies

The next major study, done by Bell Laboratories for the Psycho-Acoustic Laboratory of Harvard University, was the effect of sound and blast pressures on the eardrums of animal subjects.

The eardrum pictures were made by first removing a section of the head of an anesthetized guinea pig or cat, in order to observe the ear canal, the hammer and the eardrum. The first experiments consisted of the destruction of the eardrum by firing a 22-blank cartridge in close proximity to the animal's ear. The eardrum disintegrated and certain deafness would be the result. Since the cat's ear is very similar to that of the human ear, these studies were valuable in studying the effect of blast pressures on military personnel.

A 50-cycle note was emitted beginning with zero intensity and going to 10 db above painful sound (that is, as far as the human is concerned). It is obvious from these pictures that the distortion of the eardrum that occurs under high levels of sound, would produce extreme pain. The sound was also started at 10 db above painful sound and decreased to zero level. Extensive measurements were made from the films with both the guinea pig and the cat. (It was hoped that a cadaver would have been available to conduct similar experiments on humans, but at the time no subjects were available).

PHOTOGRAPHIC SCIENCE AND TECHNIQUE

Heart Motion Photography

Almost simultaneously with these experiments, Dr. Myron Prinzmetal at the Cedars of Lebanon Hospital in Los Angeles photographed dogs' hearts with a high-speed camera. He was interested in the effect of circulation within the heart, and took pictures at 64 frames per second with a standard camera, and at 500 and 1000 pictures per second with a high-speed camera. In making these studies, fluorescein dye was injected into the heart or into the blood stream to show the blood flow. Later studies were made on the effect of fibrillation, arrhythmias, normal sinus rhythm, and the auricles and ventricles, as well as the effect of drugs on the heart. Over the period of years in which these experiments were conducted, much valuable data was gained and when these were tied in with oscillographic records and cardiograms, a whole new understanding of the action of the human heart was instituted. A comparatively recent development in the technique of the photography of the heart was to place a mirror in one corner of the field so that the visible record of the cardiograph could be photographed simultaneously with the action of the heart without obstructing the view of the salient portions under study. (Extreme care was used to be sure that the distance from the cardiograph to the mirror to the lens was equal to the distance from the heart to the lens, to insure sharp focus of both.)

Dr. Prinzmetal's work has been done with color film exclusively and in this work he was ably assisted by Mr. John Bishop and Mrs. Eleanor Gerlach at the Institute of Medical Research. It is to be noted that all of the work done here was with lights which had not been cooled by water, and as many as twenty 750-watt photographic lamps would be focused on the subject. It is obvious that burning of the tissue would take place in time and, hence, these experiments were not conducted on humans.

Using water-cooled focusing spotlights, human heart pictures were made at St. Clair's Hospital in New York in April 1952. These pictures were made with the lights approximately 8 feet from the subject. The four lamps were focused on to a 2" x 3" area. Sequences were made during various stages of the operation and from these first experiments the results were very gratifying. Dr. Prinzmetal and his assistants are now going to use this technique in their photography of the human heart at the Cedars of Lebanon Hospital. The human heart pictures were made through the courtesy of Doctors John Madden and John Lore.

Human heart pictures, or most medical motion pictures, are made with a lens of moderately long focal length, such as 6- or 4-inch lenses. This allows ample working space for the medical personnel. In the human heart series, at one stage of the operation, hemorrhage started and the surgeon was able to immediately go in to stop the excessive flow of blood. There was no obstruction whatsoever between him and the patient.

Muscular Motion Analysis by Photography

Muscular studies and reaction times can also be studied effectively with a high-speed camera. High-speed photographs have been made in extreme close ups of the wink of the eye and of the rolling of the eyeball in normal

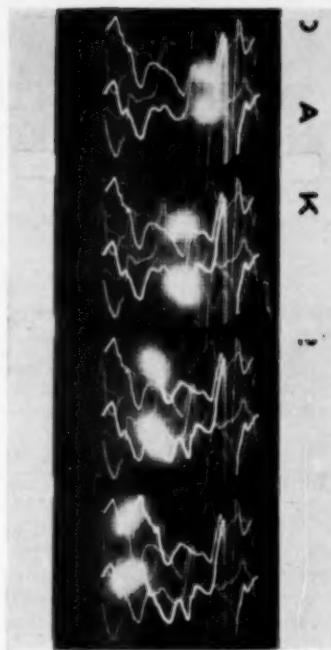


Fig. 3. Oscillographic traces from electrocardiographic fluctuations recorded by a 16mm high-speed motion picture camera for comparison with simultaneous high-speed pictures of the heart itself.

and abnormal eyes. The Institute of Medical Research is going to start a series of studies on hypertension using a high-speed camera to show the flow of blood through the superficial capillaries in the eye.

For the sequences on the eye movements two 1000-watt, 100-volt lamps were focused on the eye. The subject did not look at the lights but slightly away from them, otherwise harm to the visual mechanism might have occurred. The water-cooled lights used were such that there was no noticeable increase in temperature at the image of the filament when the hand was placed in front of them.

The effect of muscular studies and the study of animal reaction time have been observed in the frog. For this series it was hoped that the frog would jump when startled by the intense incandescent light used for high-speed pictures, but the only thing he did was blink his eyes. When pushed with a finger he just fell on his face. When jammed with a needle he did eventually jump. When shocked by a mild electric current, however, the take-off was immediate. Other motion studies have been made of a ballet dancer. These were of value to the anatomist and could be of value to students of the dance and art, since single frames can be analyzed at leisure.

There is an increasing interest in high-speed photography in medicine. This in time will, undoubtedly, become one of the most widely used analytical instruments in the study of motion, just as it is now used extensively in engineering, in manufacturing and research.

Those who are interested in studying the effect of high-speed photography in medicine will find the book, "The Auricular Arrhythmias," by Doctors Myron Prinzmetal, Eliot Corday, Isidor C. Brill, Robert W. Orlath and H. E. Kruger valuable. It is the first of its kind, in which the author calls on high-speed photography as a means of analysis. It is foreseen that this book is just the beginning and many more will follow.

SOME DESIGN FEATURES OF A WIDE-FILM CONTINUOUS PROCESSING MACHINE

J. S. Goldhammer*

ABSTRACT

The Air Force Type A-9 Processing Machine achieves high capacity and flexibility through the application of unusual design features combined with elements of conventional nature. The processing machine is 10 feet long, including the drier. However, aerial film can be immersion-processed at 20 feet per minute in normal D-19 developer used at 85F and without supplementary hardening. Eventual complete replacement of batch type film processing and mass printing on sheet paper become possible as a result of the introduction of this machine.

FOR PROCESSING aerial film and prints therefrom, American military practice has been based upon the use of the Fairchild-Smith reel-type developing apparatus and its variations (see Figure 1). In the period preceding the Normandy invasion in World War II, when it became necessary to produce vast quantities of aerial reconnaissance photographs, the inadequacies of the conventional equipment first made themselves felt. At that time no continuous processing equipment was available to the American forces other than the Kodak Ltd. Film Processor and the Williamson Multiprinter used by the British Royal Air Force (see Figure 2). Despite the relatively great bulk and low production capability of these early machines (compared to presently available equipment) the RAF units were able to outproduce American units consistently and with less expenditure of manpower.

As a result of the performance of these early British machines, the basic philosophy guiding the choice of batch-type USAF equipment was first questioned. Consequently development was initiated on the Type A-7 Processing Machine (see Figure 3). Based on the assumption that USAF photographic operations would be conducted in fixed base laboratories, a rather large machine was developed. While successful in operation, the Type A-7 Processing Machine was too large for use, being suitable only for the inter-continental RB-36

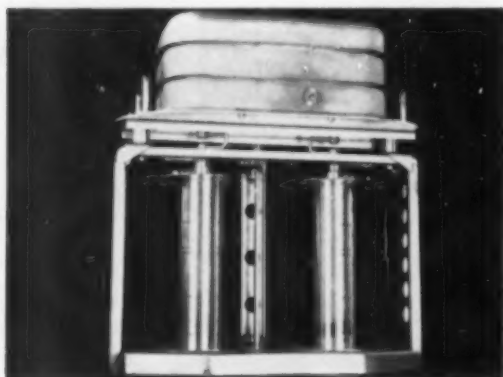


Fig. 1. Wind and rewind type B-6 developing equipment based on the Smith-Fairchild Aerial Film Developing Reel.

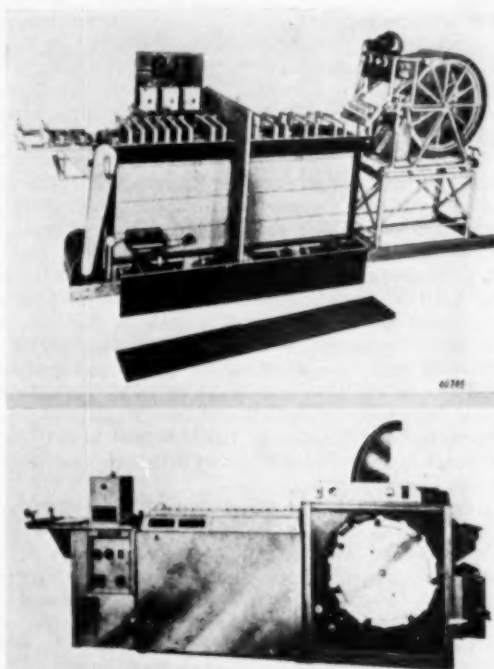


Fig. 2. Continuous film processor built by Kodak Ltd. and Williamson "Multiprinter"; both used by the RAF in Great Britain during World War Two.

organizations of the Strategic Air Command, leaving the problems of the smaller Tactical Air Command units unanswered.

A re-examination of the problems followed and it was decided that the best solution to USAF requirements would be a machine of such dimensions and capacity that one unit would be adequate for the requirements of the smallest processing laboratories in the Air Force while the number of units required by the largest laboratories would not exceed a reasonable figure; perhaps ten.

* Department of the Air Force, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio. Presented at the PSA National Convention in New York, N. Y. 16 August 1952. Received 25 July 1952.

This was the requirement, arrived at in 1948, which resulted in the current A-9 processing machine.

From an examination of the operation of British units, it was decided that the machine should be capable of either film or paper processing. Such equipment would lend great flexibility to an organization, in order to deal with changing workloads. In addition, training, maintenance and supply problems for parallel equipment would be eased.

Next, it was considered necessary that weight be held to a minimum since the equipment had to be air-portable. Dimensions also had to be held down, since an installation in an air portable semi-trailer was considered necessary for the use of Tactical Photo Units assigned to ground-support operations.

Another important consideration was power consumption. In this connection, the weight of the processing system had to be considered. Attention was given to the size of the processing machine plus power source, plus fuel to generate power, plus shelter, plus vehicles to move the system, either through the air or overland.

To recapitulate, the major design considerations were the following:

1. Adaptability to film or paper
2. Minimum weight
3. Dimensions suitable for trailer installation
4. Power consumption, as related to system weight

In addition, the usual considerations of ease of operation, serviceability, ruggedness, corrosion resistance, and parts interchangeability were considered.

With regard to film or paper adaptability, the major problem lay in the fact that the aerial film developing time at 68F is about 10 minutes in undiluted D-19 developer while the development time for bromide paper in D-72 diluted 3:1 is about 2 minutes at the same tem-



Fig. 4. Plan for semi-trailer containing two USAF A-9 processing units, one against each side.

perature. It thus became obvious that a two-speed drive was a necessity. Upon further consideration, it was decided that a variable speed drive was a better solution since it would permit time-temperature control of development and reduce the necessity for close control of solution temperature.

Disadvantages of Spray Systems

From the standpoint of minimum weight, a high temperature spray machine appeared attractive. However, several disadvantages became apparent. First, and most serious, was the fact that the required heat exchangers and pumps consumed so much power, as compared to an immersion machine, that the amount of weight removed from the machine was put back three-fold into the generator. In short, a high temperature spray machine is justifiable for a permanent installation only if the cost of power is lower than the cost of additional floor space required for an immersion machine of equivalent output. In addition, even if the total bulk could be brought down, the additional mechanical complexity would constitute a servicing problem in the field. Finally, a spray machine would require carefully filtered water, in order to prevent clogging of the nozzles. Thus horsepower required in the field for the water supply pump would be increased. If unfiltered water were to be used, either large sedimentation tanks would be required or jets of non-clogging design would be needed. However, such jets would require greater horsepower than jets of small bore operating with filtered solutions.

The decision was made to select an immersion type machine but to attempt to decrease its dimensions and weight as compared to previous designs. As previously stated, dimensions had to be held to those suitable for trailer installation. In a trailer, headroom is generally adequate, width is modest, and length is critical. In order to conserve width, it was decided that one side of the machine should be "blind"—that is, requiring no access during operation. This arrangement permitted pushing the machine against the trailer sidewall, as shown in Figure 4. Thus, two machines could be mounted in each vehicle.

In order to make use of the fact that the available vertical height was more generous than horizontal length, rather deep tanks were employed. Every attention was given to decreasing overall length and in this connection, one of those "lucky breaks" occurred which can only be ascribed to a Kindly Providence.

Optimum Roller Diameter

All previous processing machines used rather large diameter rollers, ranging from 1-3/4 to 2-1/4 inches, with



Fig. 3. The USAF Type A-7 Processing Machine, designed for use in base laboratories, complete with D-1 printer unit attached.

corresponding top roller center distances from $3\frac{1}{2}$ to over 5 inches. These diameters were believed to be over-generous, and smaller diameter rollers could be employed, it seemed, without fear of slippage or hung-up splices. After some examination of aerial camera design details, it was decided to specify 1 inch rollers on $2\frac{1}{4}$ inch centers for the prototype A-9 machine. The detail design was such that new roller guides with other center distances could be installed, if needed, and the production machine then either lengthened or slowed down to operate with larger diameter rollers on greater center distances. The designers felt sure that one inch was too small, and planned to increase roller diameters by $\frac{1}{8}$ inch increments until the minimum workable diameter was found. When the prototype was put into operation, no difficulty was experienced! It was then decided to examine the possibility of further reduction in diameter. However, when $\frac{7}{8}$ inch diameter rollers were tried, splices were not sufficiently flexible to pass over without hanging up. The designers thus earned an entirely unmerited reputation for either sagacity or occult powers.

Solution Temperature Control

The next problem to be considered was temperature control. The previous U. S. Air Force attempts at a continuous processing machine had utilized temperature control by recirculation and tempering of the developing and fixing solutions. Difficulties were encountered with leaky fittings, leaky pumps, sedimentation and crystallization in heat exchangers due to failure to rinse out with water, etc. As a result, it was decided to control temperature of the A-9 unit by means of a water jacket on the machine, rather than an auxiliary heat exchanger. Next, a choice had to be made between installing the temperature control equipment in the processing machine itself or as a separate unit. The latter course was chosen for two reasons; first, the temperature control equipment constituted the greatest mechanical complexity of the system, and therefore, the greatest potential source of difficulty. By making it a separate unit, a laboratory with several A-9s could operate with

only one spare temperature control unit. Second, the bulk of the machine could be reduced and the temperature control equipment located in areas unsuitable as working space (In the trailer installation the temperature control unit is mounted below the film drier).

Another question that had to be resolved was whether the machine should be darkroom operated or not. This question has several facets. First is the questionable availability of darkroom space in a combat zone. Second is the problem of a darkroom with several A-9s, requiring lights to make repairs if one of them went out of service. Third is the problem of designing daylight hoods that would permit access to the film to check tracking, development, etc.

After analysis of these problems, it was decided that darkroom operation, (or safelight, in the case of paper) was preferable, whenever possible, since it permitted ready access to check tracking, repair splice breaks, etc. However, provision had to be made for trailer use, commandeered space which could not be blacked out, and running repairs. Therefore, readily removable hoods and an enclosed supply magazine were provided. However, the wash tank is not hooded, so that film may be checked for operating speed, degree of development, and tracking prior to drying.

Film and Paper Drying Facilities

The next problem to be resolved was the film drying provision. More processing machines have limitations in this feature than anywhere else. The standard Air Force drier is the Type A-10A, as shown in Figure 5. It has been in disfavor since its predecessor, the A-5, was developed in the late 1930's. The unit does not "look" right on paper. It is not very efficient, thermally speaking (having about 40% efficiency). It is bulky and has a lot of parts. Nevertheless, after almost twenty years of trying to come up with a better design, including tests of vacuum driers, refrigerating and chemical dehumidifier systems, infra-red, ultrasonics, and induction heating, the USAF still has the A-10A.

It was decided to use the A-10A type drier with the A-9 Processing Machine but to make it a separate unit (see Figure 6) so that it could later be replaced, perhaps, with a more efficient unit. This decision introduced the problem of speed synchronization between the processor and the drier, since both units have variable speed drives. A very simple arrangement was worked out avoiding the complexity of an electronic control such as a Thyatron system. The system works as follows: The last dip rod in the wash section of the A-9 unit is free to rise and fall. At the top, a toggle switch is located which is turned "on" by the weight of the dip rod in the down position and turned "off" by a collar on the dip rod shaft, set at about 18 inches rise of the dip rod. First, the variable drive of the drier is set at a speed definitely higher than the processor speed. At this setting, the last dip rod in the processor rises; the drier speed is then reduced until the rate of rise is almost imperceptible. Synchronization has then been virtually accomplished. When the dip rod rises to the "off" position, the drier drive is stopped, while the processor continues to reform this last loop. When the dip rod is completely down, the drier drive starts again. In prac-



Fig. 5. Type A-10A Air Force Drier, developed from the Smith-Fairchild unit of the late 1930's.



Fig. 6. Complete A-9 processing unit coupled with USAF A-14 Drier.

tice, the drier overspeeds the processor by about 3 inches per minute or so, thus exhausting the 36 inch loop in about 12 minutes and replenishing it in 10 to 30 seconds, depending on processor speed. No harmful effects to film or paper occur in the drier, since the blower continues to operate while the forward motion is stopped.

Engineering Details of the Processor

Some idea of the physical dimensions, weight, and power requirements of the A-9 unit may be obtained from the following list of particulars.

Dimensions

The A-9 unit is 20 inches wide, 76 inches long, and 50 inches high. The operating headroom is 6 feet 4 inches, using jointed dip rods, or 9 feet if solid dip rods are used. The drier used with the A-9 unit is 24 inches wide, 40 inches high, and 42 inches long. The B-1 Temperature Control unit is 24 inches wide, 28 inches high, and 36 inches long.

Power Consumption

A-9 Processing Machine	5000 watts, 115 volts
A-14 Drier	6000 watts, 115 or 230 volts
B-1 Temperature Control	1700 watts, 115 volts

Tank Capacity

Developer	—30 gallons
Short Stop (or rinse)	—6 gallons
Fixer	—30 gallons
Wash water flow rate	— 6 gal./min. at 6 FPM 12 gal./min. at 15 FPM

Design Details

The A-9 Processing Machine is driven by a Vickers Hydraulic variable speed transmission through stainless roller chain. A hand crank is installed in the drive system for emergency operation in case of power failure. When the retractable crank is extended it declutches the power unit and engages the manual drive. All top rollers are mounted in stainless steel, enclosed, ball bearings and are driven by the roller chain through adjustable friction clutches similar to the clutches used on the Houston-Fearless motion picture film processing machines. Clutch tension is adjusted by tightening lock-

nuts on the shaft ends, which bear against helical springs, thus increasing pressure on the clutch facings. The rollers are "Uscolite" with a very slight crown and are mounted on stainless steel shafts.

Type 304 stainless steel, spot and seam welded, is used throughout. The machine is built on a channel and angle framework. Tanks, hoods, and sheathing are stainless steel. Piping is either stainless steel or polyvinyl chloride plastic material, with Hills-McCanna diaphragm valves.

Weight

The machine weighs 900 pounds dry but in operating condition and has a floor loading of 100 pounds per square foot, dry, or 200 pounds per square foot with tanks filled. The A-14 Drier weighs 400 pounds and the B-1 Temperature Control weighs 450 pounds.

Operating Characteristics

As previously stated, the A-9 Processor is capable of handling either film or paper and, between the variable speed drive and individually controllable dip rods, a wide variety of processing times can be provided. The machine has 5 dip rods in the developer tank, one short stop (or rinse) station, 5 fix and 8 wash dip rods, including the floating dip rod previously described—all others are locked, at a predetermined depth when operating. Since these dip rods form loops 8 feet in length when fully depressed, the path is as follows:

Developer	40 ft.
Short Stop	8 ft.
Fixer	40 ft.
Wash	64 ft.

In addition, a dry box between the magazine and developer tank of 24 feet capacity, is provided to permit continuous running while splicing on a new roll.

Operating at 72 F, with 9 minutes development in D-19, aerial film may be processed to gamma 1.4 at about 4-1/2 FPM. If a lower contrast is satisfactory, speed may be increased to a maximum of about 8 FPM at gamma 1.0. Operating at 85 F without prehardening baths or additives to the basic D-19 formula, gamma 1.4 can be realized at about 10 FPM, gamma 1.0 at about 18 FPM. Some fears were originally expressed about the machine's operating capability at high temperatures, but extensive tests have revealed no damage to emulsions at temperatures as high as 92F. However, the limiting factor on the system is the drier capacity, which is about 13 FPM with standard film. Recently the Eastman Kodak Company has submitted production samples of a pre-hardened film which is easier to dry, since it absorbs less moisture in processing. With this film, the drier capacity would be increased to almost 25 FPM, permitting a safe processing rate of 20 FPM, for a gamma of 1.0 at 90F.

With regard to paper processing, using D-72 diluted 3:1, satisfactory results are obtained at 72F with about 90 seconds development. This permits a maximum rate of 25 FPM. Normally, paper is run at 16-18 FPM, so that development can be increased to 2 minutes, where necessary. Increased temperature processing of paper is not too satisfactory because excessive foaming is encountered.

In connection with paper processing, the A-9 is restricted to the processing of waterproof papers for two reasons. First, non waterproof paper stretches quite badly in the developer and shrinks in the fixer. Uneven tensions, resulting in slippage, are produced. Second, the processing rate is necessarily very low because the drier cannot eliminate quickly the quantity of water absorbed in the paper base. Thus, the added cost of the waterproof paper is more than offset by increased productivity of the machine and reduced power need.

Currently the A-9 unit is being evaluated as a color processing machine, for Aero-Ektachrome and Aero-Ektachrome Duplicating Films. The scheme envisioned is the insertion of smaller tanks within the present tank, thus creating the necessary number of tanks for the more numerous color processing steps. The original tanks are then used as a water-bath to maintain solution temperatures. A rate of $1\frac{1}{3}$ FPM is anticipated for

Aero-Ektachrome at 70 F, and $2\frac{2}{3}$ FPM for Aero Ektachrome Duplicating Film at 80F.

From the foregoing discussion it is apparent that the A-9 Processor represents a merging of past ideas with new concepts and credit is therefore due the many people connected with its development. To attempt to name all who contributed would consume much time and space; nevertheless, specific recognition is due to the design staff of the Houston-Fearless Corporation, who executed our ideas and added many of their own, and to the author's colleagues in the project, Messrs. Richard D. Fullerton, Albert Berg, Arthur J. Kjøntvedt, Lt. Howard J. Silkman, and Seymour Schreck. Recognition is also due the personnel of the Harrow Works, Kodak Ltd., to Williamson Ltd., and to the Royal Air Force of Great Britain, who were responsible for ancestors of the A-9, the Kodak Continuous Film Processor and the Williamson Multiprinter.

INFLUENCE OF QUATERNARY SALTS ON PHOTOGRAPHIC DEVELOPMENT AND THEIR EFFECTIVENESS AS CHROMATOGRAPHIC DEVELOPERS*

W. Vanselow and T. H. James

ABSTRACT

The relative effectiveness of several quaternary salts in displacing adsorbed carbocyanine and merocyanine dyes from silver bromide was determined in a chromatographic column. The effectiveness in a series of pyridinium salts increases in the order: methyl, *n*-heptyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl. The effectiveness of the quaternary salts as accelerators for photographic development increases in the same order. The effectiveness of a given quaternary ion in displacing an adsorbed merocyanine dye increases markedly when excess bromide ion is added to the solution, indicating that the bromide ion promotes adsorption of the quaternary ion.

Dodecyl pyridinium ion is an effective accelerator of photographic development by agents which act as doubly or more highly charged negative ions. It is without significant effect on development by diaminodurene, and inhibits development by some derivatives of *p*-phenylenediamine and by hydroxylamine. It may either accelerate or retard development by singly charged negative ions, depending upon the nature of the developing agent. It is without effect upon the rate of the silver-catalyzed reduction of silver ions from solution by hydroquinone and *p*-hydroxyphenylglycine, but inhibits the reduction by hydroxylamine and by some derivatives of *p*-phenylenediamine.

DEVELOPMENT BY some agents is markedly accelerated by the addition of small amounts of certain cationic dyes or other quaternary ammonium salts to the developer or by bathing the exposed film in a solution of the dye or quaternary ammonium salt before development. Lüppo-Cramer first observed this effect in some experiments with a hydroquinone developer. Both sensitizing dyes, e.g., pinacyanol and pinachrome,¹ and desensitizing dyes, e.g., phenosafranin² and pinakryptol green³ produced the effect. Lottermoser and Steudel⁴ found that *n*-dodecyl (lauryl) pyridinium bromide markedly accelerates development by hydroquinone in the early stages, and accelerates development by catechol and *p*-hydroxyphenylglycine to a somewhat smaller degree. Howe and Glassett⁵ showed that *n*-dodecyl

pyridinium bromide, *n*-dodecyl triethylammonium bromide, and *n*-dodecyl α -picolinium bromide accelerate development by hydroquinone, but not by *p*-phenylenediamine and its derivatives. Sensitive photographic emulsions to which certain quaternary ammonium compounds have been added are described by Carroll,⁶ Carroll and Spence,⁷ and Smith and Stauffer,⁸ and emulsions to which certain phosphonium and sulfonium compounds have been added, by Allen and Carroll.⁹

Lüppo-Cramer¹⁰ suggested that adsorption by the silver halide of the positively charged dye ion promotes adsorption of the developing agent and thus increases the rate of reaction. James¹¹ found that phenosafranin accelerated development by all of the developing agents tested which were active in the form of doubly charged negative ions (hydroquinone, *p*-hydroxyphenylglycine, pyrogallol, ferro-oxalate ion), but had little or no effect

* Communication No. 1519 from the Kodak Research Laboratories. Received 6 October 1952.

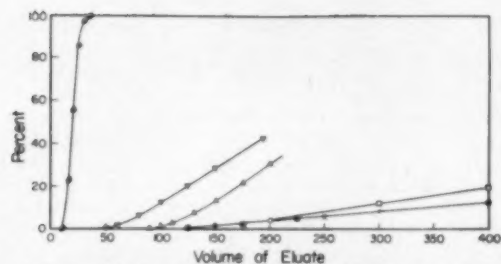


Fig. 1. Displacement of carbocyanine dye by quaternary salts. The percent of dye displaced is plotted against the volume of 0.001 M salt used. ●● = Control (Na_2SO_4); ○○ = methyl-; xx = *n*-heptyl-; □□ = *n*-nonyl-; ΔΔ = *n*-decyl-; ∇∇ = *n*-undecyl-; φφ = *n*-dodecyl pyridinium salts.

on the agents active in the un-ionized form (diaminodurene, *p*-aminodiethylaniline, *s*-dimethyl-*p*-phenylenediamine) or in the form of the singly charged ion (*p*-aminophenol, *p*-aminophenylglycine). He suggested that the negative charge barrier surrounding the silver halide grain normally prevented more than a small fraction of the doubly charged developer ions from reaching the surface because of the electrical repulsion of the negative charges. When phenosafranin is added to the developer, the positively charged dye ion is adsorbed by the silver halide, decreasing the negative charge barrier (zeta potential) and consequently increasing the fraction of the developer ions which can reach the surface. The charge effect should be much smaller when the developing agent has only a single charge, and totally absent when it has no charge. On the other hand, it should be much greater when the developing agent has three or four negative charges, and experiment showed that the accelerating action of phenosafranin¹¹ and *n*-dodecyl pyridinium ion¹² increases with the charge of the developing agent. It seems probable that the adsorbed positively charged ions act both to increase the number of developing ions reaching the surface per unit time and to promote adsorption of those ions by the silver halide grain.

The effectiveness of a positively charged ion in accelerating development should depend upon its relative adsorption by the silver halide. The greater the degree of adsorption, the greater should be the depression of the charge barrier. The relative adsorption of a series of quaternary salts can be determined by the technique of displacement chromatography which we have already used to demonstrate the adsorption of developing agents by silver bromide.¹³ We have compared the results obtained by this method with the effectiveness of the same quaternary salts in accelerating development by a triply charged agent, sodium hydroquinone monosulfonate.

The experimental procedure followed in the chromatographic determinations was the same as that previously described. Two dyes were used in the chromatographic columns, a positively charged cyanine dye, 3,3'-diethyloxycarbocyanine chloride, and an uncharged merocyanine dye, 4-[(3-ethyl-2(3H)-benzothiazolylidene)-ethylidene]-3-methyl-1-phenyl-5-pyrazolone. The chromatographic column was charged with the dye, which was adsorbed by the silver bromide, and the volume of solution of the quaternary salt required to displace the

dye from the silver bromide was determined. When the cyanine dye was used as indicator, the quaternary salts were used in water solution. The merocyanine dye was not sufficiently soluble in pure water, however, and all solutions used in experiments involving this dye were made up in a 50 percent ethanol-water mixture.

Figure 1 shows the curves representing displacement of the cyanine dye by 0.001 M solutions of methyl pyridinium methyl sulfate, *n*-heptyl pyridinium *p*-toluenesulfonate, *n*-nonyl pyridinium perchlorate, *n*-decyl pyridinium *p*-toluenesulfonate, *n*-undecyl pyridinium perchlorate, *n*-dodecyl pyridinium *p*-toluenesulfonate, and 1,2-dimethylquinolinium *p*-toluenesulfonate, with sodium sulfate as the control. The methyl and heptyl pyridinium salts give the same curve as the control, and the effectiveness of the other salts increases in the order: nonyl pyridinium, 1,2-dimethylquinolinium, *n*-decyl pyridinium, *n*-undecyl pyridinium, and *n*-dodecyl pyridinium.

In the experiments with the merocyanine dye, most of the quaternary salt solutions contained 0.001 M potassium bromide. Displacement of the dye by the quaternary salt takes place much more readily in the presence of the bromide ion than in its absence, as shown for the dodecyl pyridinium salt by curves 1 and 2, Figure 2. Curve 1 represents the displacement of the mero-

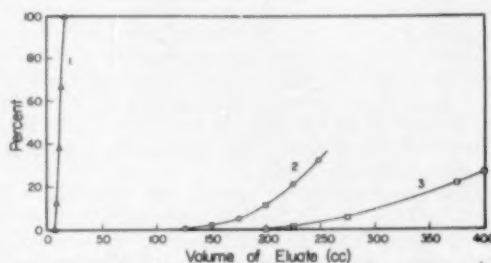


Fig. 2. Effect of bromide ion on the displacement of merocyanine dye by dodecyl pyridinium ion. Curve 1, 0.001 M dodecyl pyridinium *p*-toluenesulfonate plus 0.001 M KBr; curve 2, 0.001 M dodecyl pyridinium *p*-toluenesulfonate; curve 3, 0.001 M KBr.

cyanine dye in the presence of the bromide ion; curve 2 shows the displacement in the absence of the bromide ion. The marked increase represented by curve 1 probably arises from the influence of two factors. Bromide ion itself tends to displace the merocyanine dyes.¹⁴ The displacement of the merocyanine dye used in these experiments by 0.001 M potassium bromide is represented by curve 3. The ethanol-water solvent by itself fails to elute any dye in 400 cc. This displacement of the merocyanine dye by bromide indicates that the adsorption of dyes of this class involves some attraction between the dye and silver ion of the silver bromide. Bromide ion, which is strongly attracted by the silver ion, weakens or tends to break this bond. In addition, excess adsorbed bromide ion should promote adsorption of the quaternary ions by virtue of the attraction of oppositely charged ions. It is well known that the cyanine dyes, which are themselves quaternary salts,

are more strongly adsorbed in the presence of excess bromide ion than in its absence. Because of the attraction of the oppositely charged ions, it is probable that the combined adsorption of the quaternary ion and bromide ion by AgBr is significantly greater than that of either ion in the absence of the other.

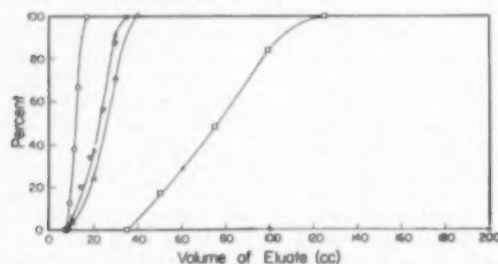


Fig. 3. Displacement of merocyanine dye by 0.001 M quaternary salts. ● = Control (KBr); △ = methyl-; ΔΔ = *n*-heptyl-; x x = *n*-nonyl-; ○ = *n*-dodecyl pyridinium salt; ∇∇ = α -picolinium- β -phenylethyl bromide.

Figure 3 shows the displacement curves of the merocyanine dye for the series of pyridinium salts. In these experiments, the quaternary salts were used in the presence of 0.001 M potassium bromide. The results obtained are in substantial agreement with those obtained with the cyanine dye. The effectiveness of the quaternary ions in displacing the dye, and hence the relative adsorption of those ions, increases in the order: methyl pyridinium, *n*-heptyl pyridinium, *n*-nonyl pyridinium, and *n*-dodecyl pyridinium. Figure 3 likewise shows the displacement curve for α -picolinium- β -phenylethyl bromide, which is an effective development accelerator. The curve for this substance nearly coincides with that of the nonyl pyridinium salt.

Photographic tests were carried out with the triply charged sodium hydroquinone monosulfonate as developing agent and a high-contrast, motion-picture positive film as photographic material. The developing solution consisted of 0.005 M developing agent buffered at pH 9.6 with sodium metaborate. The solution was prepared and used in an atmosphere of nitrogen, as described in a previous paper.¹¹ Figure 4 shows the density-time of development curves obtained at one exposure level with the developer alone and in the presence of 0.001 M quaternary salt. It is seen that the quaternary salts markedly accelerate development, and that their effectiveness in this respect places them in the same order as their effectiveness in displacing adsorbed dye from silver bromide. Hence, their effectiveness in accelerating development parallels their relative adsorption by silver bromide.

Howe and Glassett⁸ noted that development by derivatives of *p*-phenylenediamine was not accelerated by the quaternary salts. This result is as anticipated from the charge-barrier theory of acceleration of development by the quaternary salt. Indeed, it might be anticipated that the more strongly adsorbed quaternary salts would interfere with development by the uncharged agents because of competition for the adsorption sites. Our experience shows that the quaternary salts may decrease the rate of development by such agents, and by certain others as well. Table I shows some results ob-

Table I

EFFECT OF *n*-DODECYL PYRIDINIUM *p*-TOLUENESULFONATE ON THE RATE OF DEVELOPMENT BY VARIOUS AGENTS

Developer	Exposure log E	$t(0.2)$	t/t'	$t(0.6)$	t/t'	$t(1.0)$	t/t'
Diaminodurene	1.9	0.6	1.20	2.9	1.04	6.1	1.02
	1.15	.8	1.14	3.5	1.03	7.1	1.00
	.55	1.2	1.09	5.1	1.02	10.0	.99
<i>p</i> -Dimethyl- <i>p</i> -phenylenediamine	1.9	0.4	0.67	1.6	0.69	3.5	0.70
	1.15	.5	.63	2.0	.67	4.2	.69
	.55	.8	.73	2.6	.68	5.2	.63
<i>p</i> -Amino- phenol	1.9	0.4	2.5	1.0	1.00	1.75	0.6
	1.15	.55	2.2	1.35	0.76
	.55	.9	1.8
Hydroxyl- amine	1.9	2.8	0.12	3.9	0.04
	1.15	4	.07	6
	.55
<i>p</i> -Amino- phenyl- glycine	1.9	3.3	0.55	5.6	0.65	8.4	0.73
	1.15	4.9	.6	9.1	.76
	.55	7.6	.7
Catechol	1.9	0.2	2.0	0.75	1.25	1.45	1.00
	1.15	.4	1.9	1.05	1.05	2.2	.84
	.55	.6	1.9	2.15	.9
Hydroquinone	1.9	6.6	47.0	7.7	12.0	8.7	5.0
	1.15	9.5	47	11.1	13
	.55	14.3	51
<i>p</i> -Hydroxy- phenyl- glycine	1.9	24.0	40.0	27.0	14.0	30.0	7.5
	1.15	32	36	36.5	14	39	6
	.55	41	31	47	14
Ferro-oxalate	1.9	8.2	10.0	14.0	5.4	18.0	3.6
	1.15	11.5	10	18.1	5.3	23	3.9
	.55	18.2	11	27.8	5.7
Metol mono- sulfonic acid	1.9	2.8	5.6	5.6	2.0
	1.15	4.4	5	9.2	2.2
	.55	7.7	5.1

tained with various developing agents in the presence of *n*-dodecyl pyridinium *p*-toluenesulfonate. The developing solution had the composition: developing agent, 0.002 M; KOH, 0.0667 M; KBr, 0.0033 M. When the quaternary salt was present, it was in a concentration of 0.0008 M. A motion-picture positive film was used, and all development operations were at 20°C. There were two exceptions to the above developing solution composition: diaminodurene was used in 0.0014 M solution, and ferrous oxalate was used in acid solution containing 0.048 M excess potassium oxalate at pH 4.0. The values of t listed in columns 2, 4, and 6 of the table represent the times required to obtain densities of 0.20, 0.60, and 1.0, respectively, using the developer in the absence of the quaternary salt. The ratio t/t' is the ratio of the time required to obtain a given density in the absence and in the presence of the quaternary salt, and hence is a measure of the acceleration or retardation of development by the quaternary salt.

Development by diaminodurene is essentially unaffected by the presence of the quaternary salt. Development by the uncharged *p*-dimethyl-*p*-phenylenediamine and by the singly charged *p*-aminophenylglycine is retarded, and development by hydroxylamine is very markedly retarded by the quaternary salt. Development by the singly charged *p*-aminophenol is accelerated in the early stages and retarded in the later stages by the

quaternary salt. Development by the doubly charged hydroquinone, *p*-hydroxyphenylglycine, metol monosulfonic acid, and ferrous oxalate is markedly accelerated by the quaternary salt, particularly in the early stages.

It seems likely that the rather strongly adsorbed quaternary salts may actually interfere with adsorption of hydroxylamine and of some of the derivatives of *p*-phenylenediamine by silver bromide. Hydroxylamine in particular is only weakly adsorbed by silver bromide. If hydroxylamine is adsorbed by way of attachment between the silver ion and the amino group, the quaternary salt could prevent effective adsorption of the hydroxylamine even though the molecule bore a negative charge. However, an additional factor may be of importance in the retarding action of the quaternary salt when it occurs. The dodecyl pyridinium salt retards the rate of the silver-catalyzed reduction of silver ions in solution by certain developing agents, but not by others. The effect is illustrated for hydroxylamine by Figure 5. The solution employed in this experiment contained 0.164 gram of hydroxylamine sulfate, 5.0 cc of 0.1 M silver nitrate, 1.3 grams of sodium sulfite, 25 cc of 0.1 M borax, 2 cc. of 5 percent gum arabic, and 1 cc of a Kohlschutter silver sol in a total volume of 75 cc. The reaction was followed by measuring the evolution of nitrogen under atmospheric pressure, as described in a previous publication.¹⁵ Curve 1 of the figure represents the reaction in the absence of pyridinium salt; curve 2 shows the reaction in the presence of 0.05 gram *n*-dodecyl pyridinium *p*-toluenesulfonate. The reaction in the induction-

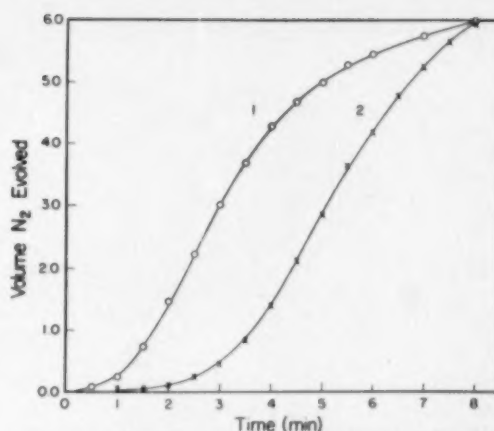


Fig. 5. Reduction of silver ions by hydroxylamine catalyzed by silver. Curve 1, no quaternary salt present; curve 2, *n*-dodecyl pyridinium *p*-toluenesulfonate added.

n-dodecyl pyridinium salt had no effect upon the rate of reduction of silver ions by hydroquinone or *p*-hydroxyphenylglycine, but decreased the rate of reduction by *p*-phenylenediamine to about 0.25 of its value in the absence of the quaternary salt, and decreased the rate of reduction by *s*-dimethyl-*p*-phenylenediamine to about 0.025 of its value in the absence of the quaternary salt. Kinetic studies of the silver-catalyzed reduction of silver ions by these agents indicate that adsorption of hydroxylamine and the *p*-phenylenediamines by silver is an important factor in the catalysis. It seems likely that the inhibition of the reaction by the quaternary salts is the result of adsorption of the quaternary salt interfering with adsorption of the developing agent. The kinetic studies have given no indication of adsorption of hydroquinone by silver, and the quaternary salt does not inhibit this reaction.

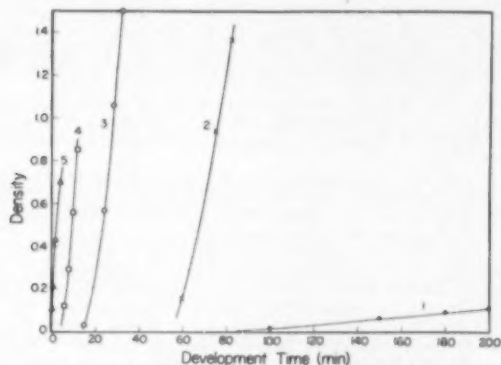


Fig. 4. Effect of quaternary salts on development by sodium hydroquinone monosulfonate at pH 9.6. Curve 1, no addition; curve 2, 0.001 M *n*-heptyl pyridinium *p*-toluenesulfonate; curve 3, 0.001 M *n*-nonyl pyridinium *p*-toluenesulfonate; curve 4, 0.001 M 1,2-dimethyl-quinolinium *p*-toluenesulfonate; curve 5, 0.001 M *n*-dodecyl pyridinium *p*-toluenesulfonate.

period stage is greatly retarded by the pyridinium salt. Beyond the induction period, the salt has little effect upon the reaction rate. Similar experiments were carried out with other developing agents, using optical density as a measure of the course of the reaction. The

Bibliography

1. H. Lüppo-Cramer, *Kolloid Z.*, Vol. 18, p. 163 (1916).
2. H. Lüppo-Cramer, "Negativ-Entwicklung bei hellem Lichte," 2nd edition, E. Liesegang, Leipzig, 1922, p. 101.
3. H. Lüppo-Cramer, *Phot. Korr.*, Vol. 63, p. 242 (1927).
4. A. Lottemoser and R. Steudel, *Kolloid Z.*, Vol. 82, p. 319 (1938); Vol. 83, p. 37 (1938).
5. D. J. T. Howe and J. W. Glassett, *Brit. Pat.* 566,314 (1944).
6. B. H. Carroll, U. S. Pat. 2,271,623 (1942).
7. B. H. Carroll and J. Spence, U. S. Pat. 2,334,864 (1943).
8. W. F. Smith and R. E. Stauffer, U. S. Pat. 2,410,690 (1943).
9. C. F. H. Allen and B. H. Carroll, U. S. Pat. 2,271,622; 2,275,727; 2,288,226 (1942).
10. H. Lüppo-Cramer, *Phot. Korr.*, Vol. 75, p. 81 (1939).
11. T. H. James, *J. Phys. Chem.*, Vol. 43, p. 701 (1939).
12. T. H. James, *J. Phys. and Colloid Chem.*, Vol. 55, p. 563 (1951).
13. T. H. James and W. Vanselow, *J. Am. Chem. Soc.*, Vol. 73, p. 5617 (1951); Vol. 74, p. 2374 (1952).
14. T. H. James and W. Vanselow, *Sci. ind. phot.*, in press.
15. T. H. James, *J. Am. Chem. Soc.*, Vol. 61, p. 2379 (1939).

BOOKS RECEIVED

COLOR IN BUSINESS, SCIENCE, AND INDUSTRY by Deane B. Judd, John Wiley & Sons, Inc., New York 16, N. Y. (1952), 401 pages, \$6.50.

This is a practical book for the technical man in business and industry, or the scientific worker, to whom color problems are frequent occurrences but not his main concern. It provides ready reference material on color characteristics, measurement, reproduction, standards, classification and terminology.

The basic facts of color perception are covered in the 62 pages of Part I. This prepares the otherwise uninformed reader to understand and make use of the information presented in the remaining 323 pages of text and illustrations. These basic facts include anatomy and function of the human eye and its relation to the overriding effect of the interpretations given by the brain to what the eye sees.

Part I also treats psychology of color as applied to the customer for the benefit of readers engaged in business and industry. Consideration is given to color blindness and its influence on the customer as well as on the manufacturer's inspector.

Part II, the largest of the three parts, is devoted to the tools and techniques of measuring, reporting, and interpreting color data. The General Electric Recording Spectrophotometer and the Beckman Quartz Spectrophotometer, the two most useful tools for measuring and recording the colors of objects, are rather completely described and the prospective client for industrial color control may form an opinion as to which of these, or other measuring methods, will most adequately meet his requirements. In this part of the book the reader benefits from the long experience of Dr. Judd, both in industry, and at the National Bureau of Standards where a wide variety of color measuring problems have been dealt with over the years.

The ICI Standard Observer and Coordinate System of expressing color values, along with its shortcomings and the possible trend to be taken in the future to overcome them, are presented. The book tells, for example, how to reduce spectrophotometric data to tristimulus values, one of the many practical discussions presented concisely for the person who requires means of expressing and controlling color but who cannot make this very interesting field his life's work. The practical possibilities, as well as the shortcomings of visual colorimeters are included in the treatment of tools and techniques.

Color television is used as the example for the section of the book devoted to the treatment of reproduction of pictures in color, and the reader is led to associate the problems of color reproduction in printing and in photography with those found in our youngest color reproduction process.

The preparation and maintenance of color standards in the paint industry is a typical color problem treated by the author. Many of the variables may be controlled by the spectrophotometer, but the task of matching previous colors has yet to be relieved by direct measuring methods. Many of the color standards are presented and illustrated in Part II of Dr. Judd's book with a thoroughness that gives the reader a pretty good idea of what he may expect in the way of standardization in his own particular color problem.

A very valuable section at the end of Part II treats the subject of terminology of color with a discussion, listing and definitions of general terms—Ostwald terms, Munsell terms, physical terms, chemical terms, colorant terms, names of colors and abbreviations for ISCC-NBS designations are given.

The last part, III, deals with physics and psychophysics of colorant layers, which is really the influence of the material nature of the colorant on the observer's interpretation. The author goes into the properties of the materials that effect their apparent color. These include surface gloss, structure, thickness, opacity or hiding power, etc., and they are the properties the proper understanding of which forms the art of "know-how" in color manufacturing.

Throughout his book Dr. Judd has been careful not to get into technical discussions that would leave his non-technical reader behind. The book is short, considering the volume of material that now exists in the field of color, and the author has condensed the important features of this science into a handbook that promises to be extremely useful to those who want to understand the nature of certain color problems with the least study and research.

IRA B. CURRENT

PHOTOGRAPHY IN HIGHWAY RESEARCH

Literature References for Mr. Allie C. Peed, Jr.'s paper on this subject, inadvertently omitted from our October 1952 issue, are printed below for the information of our readers. Ed.

References

1. Havens, James H., and Peed, Allie C., Jr., Kentucky Department of Highways, "Spherical Lens Optics Applied to Retro-Directive Reflection." Presented at the 31st Annual Meeting of the Highway Research Board, Washington, D. C., January 1952. To be published.
2. Rhodes, C. C., and Pocock, B. W., Michigan Department of Highways, "A Discussion of the Principles of Glass Bead Reflectorization." Presented at the 31st Annual Meeting of the Highway Research Board, Washington, D. C., January 1952. To be published.
3. Havens, James H., and Goodwin, W. A., Kentucky Department of Highways, "Clay Mineralogy and Soil Stabilization." Presented at the meeting of the American Society of Civil Engineers in New York, October 1951.
4. Lyon, V. H., and Robinson, D. L., Missouri State Highway Department, "A Study of Glass Beads for Reflectorizing Traffic Paint." Proceedings of the 29th Annual Meeting of the Highway Research Board, Washington, D. C., December 1949.
5. Peed, Allie C., Jr., Kentucky Department of Highways, "A Comparative Study of the Physical Properties of Traffic Paints." Presented at the 31st annual meeting of the Highway Research Board, Washington, D. C., January 1952. To be published.
6. Green, F. H., Joint Highway Research Project, Purdue University, "Method for Recording Lateral Position of Vehicles." Proceedings of the 26th Annual Meeting of the Highway Research Board, 1946.
7. Quimby, Warren S., Joint Highway Research Project, Purdue University, "Traffic Patterns at a Narrow Bridge." Proceedings of the 27th Annual Meeting of the Highway Research Board, 1947.
8. Forbes, T. W., and Reiss, Robert J., University of California Institute of Traffic and Transportation Engineering, "35 Millimeter Air Photos for the Study of Driver Behavior." Presented at the 31st annual meeting of the Highway Research Board, Washington, D. C., January 1952. To be published.
9. Greenshields, Bruch D., George Washington University, "The Potential Use of Aerial Photographs in Traffic Analysis." Proceedings of the 27th annual meeting of the Highway Research Board, 1946.
10. Jenkins, D. S., Belcher, D. J., Gregg, L. E., Woods, K. B., "The Origin, Distribution and Airphoto Identification of United States Soils." U. S. Department of Commerce, CAA, Washington, D. C., Technical Development Report No. 52, May 1946.
11. Lancaster, R. J., Bureau of Public Roads, Driscoll, J. E., The Asphalt Institute, "The Cooperative Project on Structural Design of Nonrigid Pavements." Highway Research Abstracts, April, 1949.
12. Havens, James H., and Peed, Allie C., Jr., Kentucky Department of Highways, "Field and Laboratory Evaluation of Roadside Sign Surfacing Materials." Bulletin No. 43 (1951) Highway Research Board, Washington, D. C.

PHOTOGRAPHIC SCIENCE AND TECHNIQUE

PHOTOGRAPHIC SCIENCE AND TECHNIQUE

A quarterly technical supplement to PSA Journal

TABLE OF CONTENTS — MAY 1953

SWELLING CHARACTERISTICS OF SYNTHETIC POLYMER EMULSIONS UNDER PROCESSING CONDITIONS	V. F. H. CHU, R. W. NOTTORF, AND W. H. VINTON	43
CAMERA STAND FOR CINE-PHOTOMICROGRAPHY	EDWARD H. BLOCH AND ALVAR NORDSTROM	47
SOME CONSIDERATIONS OF RESOLUTION, SHARPNESS, AND PICTURE QUALITY IN TECHNICAL PHOTOGRAPHY	DUNCAN MACDONALD	49
SHARPNESS OF PHOTOGRAPHIC IMAGES	G. C. HIGGINS AND L. A. JONES	55
PHOTOGRAPHY IN A GENERAL HOSPITAL	LEONARD A. JULIN	61
INFLUENCE OF OXYGEN AND MOISTURE ON THE HERSCHEL EFFECT	W. VANSELOW, R. F. QUIRK, AND T. H. JAMES	66
APPLICATION OF COLOR PHOTOGRAPHY TO A CLEFT LIP AND PALATE RESEARCH AND TRAINING PROGRAM	FREDERICK T. SHARP	70
POLAROID INTEROCULAR CALCULATOR	SAMUEL KITROSSER	74
MODERN PHOTOMICROGRAPHY IN BRIEF REVIEW	OSCAR W. RICHARDS	77
MATERIALS OF CONSTRUCTION FOR PHOTOGRAPHIC PROCESSING EQUIPMENT L. E. MUEHLER AND J. I. CRABTREE		79



TECHNICAL NOTES AND LETTERS

Dear Sir:

I am very much interested in Photographic Science and Technique so I will be very grateful if you would inform me whether the back numbers of the publication are still available, if so I want to buy them all. I also want to know if it is possible to enter a subscription in the name of my office, Hydrographic Office of Royal Thai Navy, but at the time being I want to have these publications sent to the above address until I notify you to send them to my office in Bangkok, Thailand.

I was being sent to the United States for further study and I have been in your country for 3 years now. I am not going back until about the end of next year. Actually, photography is not my major subject of study but since there are only a few photographers in my country who understand it scientifically, I devote my time after the regular working hours for studying photography and try to collect every kind of publications for use as reference. Our Navy also is contemplating in expanding the Photographic Unit.

Ampon Penypol
Lieutenant, Royal Thai Navy

Complete sets of Photographic Science and Technique for the years 1950-1952 inclusive are still obtainable from Society Headquarters in Philadelphia, along with the PSA Journal Section A issues with which they appeared, at a cost of \$1.00 per copy, postpaid.

Mechanism of Photographic Sensitivity

G. I. P. Levenson sent a contribution on this subject from the Scientific and Technical Group of the Royal Photographic Society of Great Britain that appeared in our February issue. After seeing it in print, he discovered that the typist had omitted one line from the communication which, although the text makes sense as it was printed, would be vastly improved if the missing words are inserted. The fifth sentence in the second paragraph should read: "As applied to latent image formation, however, the (Gurney and Mott) theory is incomplete: one has to explain *how the positive holes are prevented from recombining with the electrons* and how the first electrons are trapped if no silver is initially present."

An additional literature reference under number 4 that should prove useful to students in this field is suggested by our contributor: "Fundamental Mechanisms" page 242. Readers

who have not already made the correction should note that Dr. Levenson's middle initial is I. and not L. as shown in the February issue.

Reflecting Microscopes

Dr. Barer of Oxford University described some of his work using reflecting microscopes for ultra violet and infrared microspectroscopy at a December 18, 1952, meeting of the Scientific and Technical Group of The Royal Photographic Society of Great Britain.

The illuminating system for a reflecting microscope of this type presents difficulties, particularly with regard to the aperture stop for the condenser and in the design of a suitable monochromator. These difficulties have been satisfactorily overcome. The special monochromator now used embodies a grating, ruled to put all the light in the first order, ultraviolet spectrum and uses circular iris diaphragms instead of slits.

Since a reflecting microscope is perfectly achromatic it is possible to make adjustments visually by white light even though the work is to be done by ultraviolet light.

Reviewing alternative microscopes of other workers, Dr. Barer mentioned that it had been shown by Burch that spherical mirrors cannot be successfully employed over N.A. 0.5 and that this had been confirmed by Grey in America. There are also great disadvantages in these other systems, resulting from the high obstruction ratio of the second reflecting surface, leading to greatly reduced contrast and also to very restricted field of view. Mention was made of the refracting-reflecting spherical system of Grey, employing components made of quartz and fluorite, and also to Grey's ultraviolet colour-translating microscope. While this instrument is of great ingenuity and complexity, its practical use may be somewhat restricted. Solid optical components were also referred to, but practical instruments such as that of Bouwers are restricted to visual use only.

The first two Burch-type instruments of a batch of ten now under construction are now in use. The aspherical mirrors (of speculum metal and stainless steel) for both the condenser and the objective are identical in form and have a numerical aperture (N.A.) of 0.65. By the addition of a special immersion lens, the N.A. can be raised to 0.95 though the system is not then completely achromatic. Dr. Barer's conclusions are that the new Burch instruments are unique in their high performance and are the only instruments existing which meet all the permitted tolerances.

SECOND 1953 ISSUE



VOLUME 19B, NUMBER TWO



PUBLISHED WITH THE PSA JOURNAL FOR MAY 1953

PHOTOGRAPHIC SCIENCE AND TECHNIQUE BOARD OF EDITORS

EDITOR, PAUL ARNOLD, APSA

26 Hotchkiss Street, South Binghamton, N. Y.

ASST. EDITOR, H. LOU GIBSON, FPSA

343 State Street Rochester 4, New York

LAWRENCE B. FRIAR P.O. Box 1009 Rochester 3, New York

MORRIS GURRIE 5412 N. Bernard Street Chicago 25, Illinois

PETER KRAUSE, APSA 69 Bourndale Road, South Manhasset, New York

R. C. HAKANSON 10322 Lake Shore Boulevard Cleveland 8, Ohio

HERBERT MEYER 1421 Northwestern Avenue Hollywood 27, Calif.

HUTTON HOWELL 700 Commonwealth Avenue Boston, Massachusetts

JOHN B. TAYLOR 118 Laurel Avenue Binghamton, New York

PHOTOGRAPHIC SCIENCE AND TECHNIQUE is an official organ of the Photographic Society of America dedicated to the publication of scientific and technical papers dealing with the theory and practice of photography. Its aim is to encourage the publication of authoritative articles describing original research, techniques, and the engineering aspects of new equipment in all fields of photography. It is intended to interest and inform the advanced amateur, the professional, the technologists, and the scientists who study or apply photographic processes.

Prepared four times yearly by the Technical Division, Photographic Science and Technique is published as SECTION B of the PSA JOURNAL. The issues are separately numbered and page numbered and indexed annually.

Society memberships, including subscriptions to both publications, may be obtained from PSA Headquarters, 2005 Walnut Street, Philadelphia 3, Pennsylvania, upon payment of \$10.00 annual dues. Separate subscriptions are not available, except institutional and library subscriptions at \$5.00 a year. No extra charge is made for mailing to foreign countries.

Address all manuscripts and communications to the Editor. Unacceptable manuscripts will be returned promptly. No responsibility is assumed for the accuracy of statements by contributors but attempts will be made to avoid the publication of errors. The contents will be protected by domestic and foreign copyright and may not be reproduced without the written permission of the editor. The publishing of opinions expressed by authors does not necessarily indicate concurrence or endorsement by the editors, by the Technical Division, or by the Photographic Society of America.

Le Film de Recherche Research Film Forschungsfilm

Under this title, a new Bulletin has just appeared which is run and will be distributed at regular intervals by the Committee of the Research Film Section of the International Scientific Film Association (I.S.F.A.).

Dr. G. Wolf of Gottingen and M. Jean Dragesco of Paris are the joint editors. The Bulletin, international in scope, carries articles in English, French and German. Its aim is to cater for all those interested in the use of film as a tool in scientific research.

It is perhaps astonishing that users of film as a scientific

tool did not organize themselves until 2 1/2 years ago, when, after considerable spadework, the Research Film group of the I.S.F.A. was formed at Utrecht. The organizing committee of the Section has right from the start regarded as one of its most important tasks the systematic filing of information on the use of film in research, information which tends to be scattered over many journals.

The editors express the hope that each issue of the Bulletin will contain an illustrated original article, reviews of books, articles on the use of film in science or on films themselves, information about the activity of the Committee and bibliographical notes.

W. F. BERG

SWELLING CHARACTERISTICS OF SYNTHETIC POLYMER EMULSIONS UNDER PROCESSING CONDITIONS

V. F. H. Chu, R. W. Nottorf and W. H. Vinton*

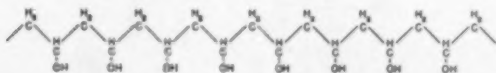
SUMMARY

The swelling of the color-forming polymer emulsion binders derived from polyvinyl alcohol and used commercially in DuPont Safety Color Release Positive Film (Type 875) is quite different from that of gelatin. Therefore, processing procedures which have been devised for photographic materials using a gelatin binder are not necessarily optimum for such synthetic binders.

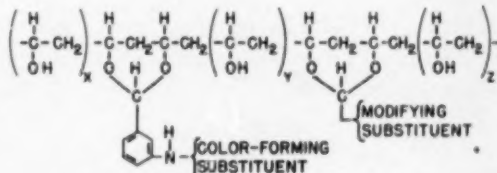
This paper deals with the swelling characteristics of polyvinyl alcohol derivatives and methods for control of such swelling. Special techniques which permit processing these binders at elevated temperatures will also be discussed.

FOR MANY years techniques have been known for processing gelatin emulsions in such a way as to control their swelling and increase their resistance to more vigorous processing conditions. This has been achieved by adding gelatin hardeners such as alum to the appropriate processing solutions, so that the final processed film is substantially different in physical properties from the starting material. Analogous techniques have been devised in these laboratories for controlling the swelling of a newer class of synthetic photographic emulsion binders. It is the purpose of this paper to describe our observations on the inherent swelling characteristics of this new class of synthetic polymers and to describe how this swelling may be controlled both in the manufacture of photographic materials employing them and in the processing of such materials.

These polymers have taken on importance in the photographic field because they are being used commercially as binders to replace gelatin in the manufacture of color photographic emulsions. The parent synthetic polymer from which the color-forming binders are derived is polyvinyl alcohol, which can be considered to have the following structure:



A generalized formula for the color-forming binders themselves can be represented as follows:



It can be seen that the original polyvinyl alcohol has been altered in two ways; first, a carefully controlled number of color-forming groups has been introduced via the formation of acetal linkages; second, a carefully controlled number of modifying substituent has been added, again through acetal linkages. In a previous paper by Jennings, Stanton and Weiss¹, a new motion picture film, DuPont Color Release Positive, was described. This product, now coated on safety base and designated as Type 875, employs three different synthetic polymers of this class. These polymers serve both as binders for the light-sensitive silver halide and as the color-forming constituents; no gelatin whatsoever is used in the film. One of the color-forming binders bears a substituent which makes it give rise to a yellow dye upon development with a suitable *p*-phenylenediamine developer; the second color-forming binder yields a magenta dye under similar conditions; while the third synthetic binder produces a cyan dye during color development.

In addition to meeting exacting chemical requirements (color coupling, sensitization and stabilization of silver halide grains), the synthetic binders have also met rigorous requirements as to their physical characteristics. In its original form as a raw material for emulsion manu-

* Technical Division, Photo Products Department, E. I. du Pont de Nemours & Co., Inc., Parlin, N. J. Presented by Dr. Vinton at the PSA National Convention, New York, N. Y., 14 August 1952. Received 3 December 1952.

facture, each of the three individual binders is soluble in a water and ethanol mixture so that emulsions can be made and coated by practical procedures. Each binder sets to a gel during coating so that a smooth emulsion layer of suitable thickness is obtained. Each binder swells enough to allow the even and rapid penetration of processing solutions but does not swell to an excessive extent nor go into solution at this stage. These characteristics have been achieved² by selection of polymers of the correct molecular weight, the introduction into the polymeric structure of the right number and kind of substituents and by steps in the manufacturing process which transform the original water-sensitive material into a less water-sensitive form. The selection of polymers is entirely in the hands of the manufacturer, but the means chosen to achieve the last step (conversion of the polymer to a less water-sensitive form) is of interest to a processor

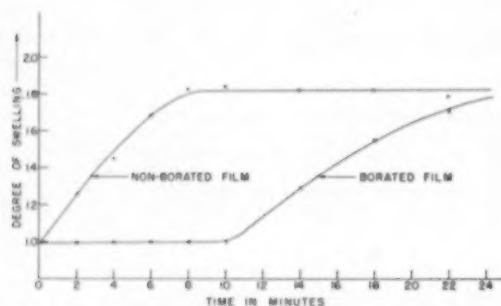
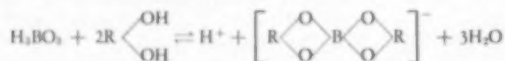


Fig. 1. Swelling of unsupported films of yellow color-forming binders in tap water at 70F.

as well as to the film manufacturer. This conversion is achieved through the chemical action of a soluble borate on the polymeric binders, accomplished at the time of the coating operation.

It has long been known that boric acid and borates form complexes with polyhydroxy compounds such as glycerol, mannitol and catechol. In the case of organic compounds containing two hydroxyl groups, symbolically represented as $R\begin{smallmatrix} \text{OH} \\ \diagup \diagdown \\ \text{OH} \end{smallmatrix}$, Böreskén and Vermaas³ proposed the following equilibrium:



According to the law of mass action, the complex should be more stable in alkaline solution than in acid, since hydrogen ion will be withdrawn from the system on the right, thus favoring complex ion formation. For similar reasons the complex will also be more stable in solutions containing higher boric acid content. Since the previously described synthetic color-forming binders contain numerous hydroxyl groups in the 1,3-position relative to one another, it is not surprising that boric acid will form complexes with such binders. The laws of probability suggest that some boric acid molecules will react with hydroxyl groups from different polymer molecules. This should transform the previous straight-

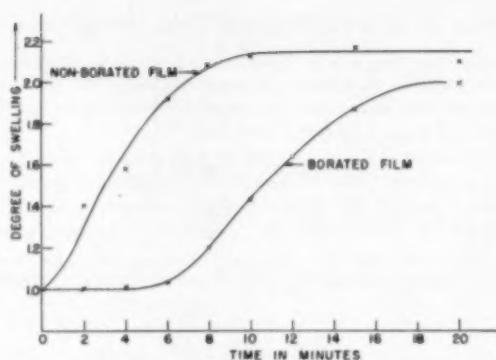


Fig. 2. Swelling of unsupported films of magenta color-forming binder containing silver halide, in tap water at 70F.

chain structure into a network configuration and should alter the physical properties of the binder, particularly by increasing its viscosity or even converting it to a gel. Films of such a cross-linked polymer should have greater wet strength and decreased tendency to swell in water and processing solutions. This change of properties with borate treatment has been observed in our laboratories. The practical result of this is a photographic binder which has a "built-in" hardener; hence under normal circumstances such a binder will require less attention to hardening treatments during processing. The ability to form a cross-linked gel is used to advantage in the manufacture of Type 875 Color Positive Film where the emulsions are set to a gel chemically by the formation of borate cross-linkages when the emulsion is applied to a special borate-treated base. This is in marked contrast to gelatin emulsions which are set to a gel structure by chilling after coating.

In order to observe quantitatively the swelling behavior of the color-forming polymers under the influence of soluble borates, the following experiments were devised. Films were prepared by coating a thin layer of a solution of soluble borate onto one-half of a level glass plate; after this solution was dried, a dilute aqueous-alcohol solution of the synthetic polymer binder was cast onto the whole glass plate in an amount

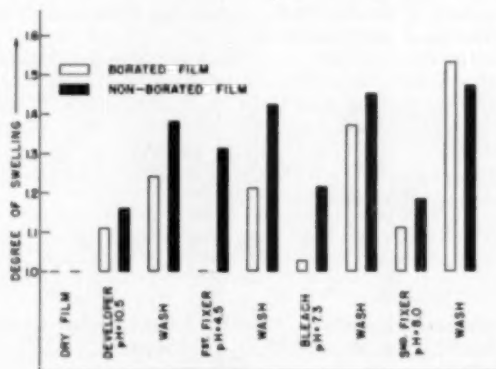


Fig. 3. Swelling of unsupported films of yellow color-forming binder during photographic processing in various solutions.

Table I

FORMULAS FOR PROCESSING TYPE 875 COLOR POSITIVE FILM

Developer		First Fixer Concentrate	
p-Aminodiethylaniline monohydrochloride..	2.5 g	Hypo, crystals.....	240 g
Sodium sulfite, anhyd..	10.0 g	Sodium sulfite, anhyd.....	15 g
Sodium carbonate, monohyd.....	47.0 g	Borax.....	18 g
Potassium bromide.....	2.0 g	Acetic acid, 28%.....	43 ml
Water to make.....	1000 ml	Potassium alum.....	20 g
pH = 10.5 (approx.)		Water to make.....	1000 ml
		pH = 4.5 (approx.)	
		For use: dilute 1 part concentrate with 2 parts water	
Bleach		Second Fixer	
Potassium ferricyanide..	100 g	Hypo, crystals.....	200 g
Boric acid.....	10 g	Water to make.....	1000 ml
Borax.....	5 g	pH = 8.0 (approx.)	
Water to make.....	1000 ml		
pH = 7.0 to 7.5			

and concentration sufficient to yield a film of about 0.003 to 0.004 inches in thickness after drying. Thus, one-half of the film contained borate cross-linkages and the other half did not. To measure the relative swelling, discs of known diameter were cut from the two halves of the film and submerged in an unsupported fashion in tap water at 70°F. for different lengths of time. A comparison of the swelling of borated and non-borated yellow color-forming binder over a 24 minute period of immersion is given in Figure 1. The increase in diameter of the films serves as a measure of the swelling. The

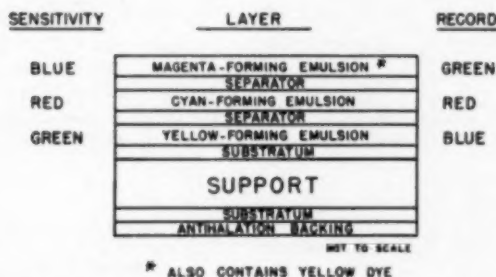


Fig. 4. Schematic diagram showing structure of DuPont Type 875 Color Positive Motion Picture Film.

"degree of swelling" is defined as the ratio of the diameter of the disc soaked in water to that of the original dry disc. Thus a "degree of swelling" of 2.0 means a doubling of the diameter. It is seen that the non-borated synthetic binder swelled very rapidly as soon as it was immersed in the water, while the borated binder swelled scarcely at all during the first 10 minutes. On prolonged soaking in water, however, the borated film did swell eventually to about the same extent as the non-borated film. This is to be expected since the cross-linked binder will gradually revert to its original form, because the boric acid in equilibrium with the complex is leached out and the equilibrium as shown in the equation is caused to move to the left.

The magenta and cyan color-forming binders have swelling behaviors and responses to borate cross-linking almost identical with the yellow color-former shown in Figure 1, although the absolute value of the swelling

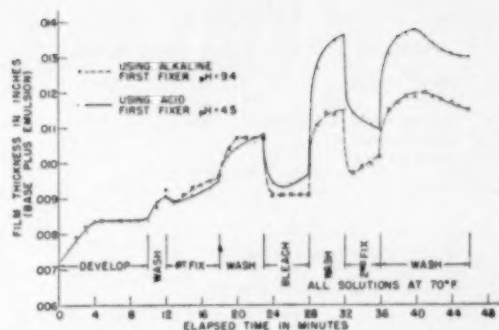


Fig. 5. Vertical swelling of multilayer color film (DuPont Type 875) during processing in various solutions.

varies slightly from polymer to polymer. This marked difference in the swelling of unsupported borated versus non-borated films is equally demonstrable for unsupported films containing silver halide in addition to the color-forming binder. Figure 2 shows the degree of swelling in tap water at 70°F. of a nonborated magenta color-forming binder containing silver halide as compared with a similar borated binder when plotted against the time of swelling (in minutes).

Having examined the lateral swelling of unsupported color-forming binders in tap water, it was then of interest to follow the swelling behavior of these unsupported binders throughout the entire processing cycle recommended for Type 875 Color Positive Film. (This cycle consists of color development, initial fixation, bleaching and a second fixation, with water washes or rinses interspersed.) The standard formulas of these solutions have been given in a previous paper¹, they are repeated here (Table I) for purposes of ready reference.

Similar borated and non-borated films of each of the three color-forming binders were prepared as previously described. Discs of each type were placed successively in the various processing solutions at 70°F. for the prescribed length of time. Swelling behavior in the case of the yellow color-forming binder is given in Figure 3. It is seen that the borated synthetic binder swelled much less during the steps from developing through bleaching. However, after that step, the two films swelled to about the same extent. The magenta and cyan color-forming binders behaved similarly. In seeking the explanation of this behavior, it should be noted that the pH values of the standard developer, bleach and second fixer were all on the alkaline side (above pH 7). The wash water was also slightly alkaline. On the other hand, the pH of the standard first fixer was strongly acid (pH 4.5). It is recalled that the borate complex is not very stable at high hydrogen ion concentration, i.e., in acid solutions. We therefore conclude that the borate cross-linkages were broken in the acid first fixer and, following this, the borate ions were washed out in processing. Thus, the degree of swelling of the borated and non-borated films eventually became the same. This is not of serious concern in normal practical processing. However, an understanding of this mechanism has led to special techniques which retain the borate cross-linkages and permit more drastic processing conditions without damage. These will be described subsequently.

Table II

FORMULA FOR ALKALINE FIRST FIXER

Hypo, crystals.....	80.0 g
Borax.....	10.0 g
Sodium sulfite, anhydrous.....	5.0 g
Glacial acetic acid.....	4.0 ml
Water to make.....	1000 ml

Adjust pH to 9.5

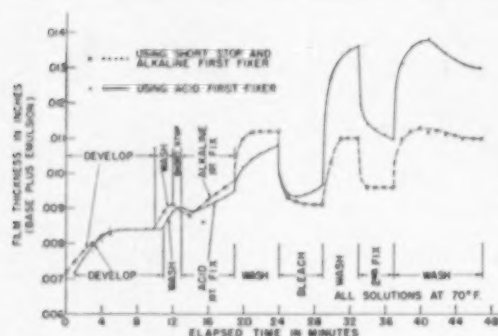


Fig. 6. Vertical swelling of multilayer color film (DuPont Type 875) during processing with special acid short stop before the alkaline fixer.

Thus far in this paper consideration has been given only to the lateral swelling of unsupported films in water and processing solution. It was of interest to know next whether these data also apply to the swelling of a multilayer coated film in a direction *perpendicular* to the film base support. For this study DuPont Safety Color Release Positive Film (Type 875) which contains borated layers of the three color-forming binders (plus other separator layers) on a safety support was selected. The total thickness of these layers is about 0.001 inches. A schematic cross section of the film structure is shown in Figure 4. The swelling of this film during the normal processing sequence was determined by measuring the total film thickness at one minute intervals by means of a micrometer. In addition to the *normal* sequence, a *modified* processing sequence was devised which used an alkaline first fixer (composition shown in Table II) rather than the conventional acid first fixer. In Figure 5 the swelling curves are given for identical samples of Type 875 Color Positive Film processed by these two different processing sequences. The sequences were identical except for the composition of the fixers. The solid curve gives the swelling obtained when an acid first fixer was used and the dotted curve that obtained when an alkaline first fixer was employed. These curves show that swelling can be further suppressed by chemical means during processing (when such suppression is desired for special purposes such as high temperature processing) by maintaining the pH of the first fixer on the alkaline side. This effect can be explained on the basis that the borate cross-links remain stable in alkaline solution. However, with only a water rinse before the first fixer, development will continue in this alkaline fixer and thus cause fogging. Thus, to make practical use of the alkaline first fixer, it is desirable to use a special acid short stop between the developer and the alkaline first fixer in order to stop development. The

Table III

FORMULA FOR ACID SHORT STOP

Disodium hydrogen phosphate, dodecahydrate.....	40.0 g
Sodium sulfite, anhydrous.....	10.0 g
Borax.....	6.0 g
Glacial acetic acid.....	40.0 ml
Water to make.....	1000 ml

Adjust pH to 4.0

composition of such a short stop is given in Table III. It will be noted that a high salt content is present; this, as will be shown later, also tends to minimize swelling. The effect of these processing modifications on the vertical swelling of Type 875 Color Positive Film is shown in Figure 6. Here it is seen that, in spite of the use of an acid short stop, the swelling of the film in the final wash remains markedly lower than that obtained through the standard sequence. This behavior can be explained in the following way. Although some borate cross-linkages are broken in the acid short stop bath, swelling is held to a minimum by the high salt content of the solution. As the film passes into the alkaline first fixer, it is presumed that the borate cross-linkages are reformed according to the original mechanism, since the loss of borate ions will have been small. Thus, if it is desired to process Type 875 at temperatures markedly above 70F, procedures similar to that just described may be used (see Table IV).

On the other hand, if the elevation in solution or wash water temperature above the normal 70F is small,

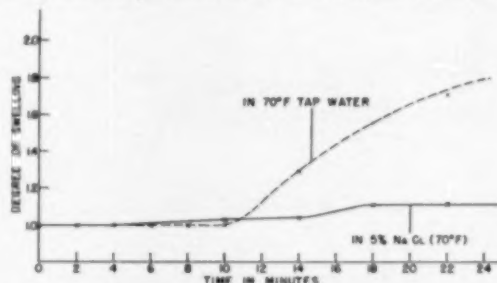


Fig. 7. Effect of salt on swelling of unsupported films of yellow color-forming binder containing borate.

a second and somewhat simpler alternative is available. This consists of the use of the standard solutions (Table I) throughout processing, except for a salt solution which replaces the water rinse following the acid first fixer. As a salt solution, 5% sodium bicarbonate is recommended, although a 5% sodium chloride solution functions equally well. The latter, however, may be more corrosive in some types of commercial processing equipment. This salt bath tends to inhibit the swelling of the color-forming polymers and thus to minimize loss of borate ions. As a result, when the film passes into the alkaline bleach which follows, the borate cross-linkages are restored.

This "salt effect" on the swelling of the synthetic color-forming binders can be demonstrated by comparing the degree of lateral swelling of an unsupported film of one of the polymers in tap water versus its swelling in

Table IV

A PROCESSING PROCEDURE FOR TYPE 875 FILM PERMITTING
USE OF HIGHER TEMPERATURES

1. Develop.....	10-12 min
2. Air blow-off.....	
3. Short stop (Table III).....	2-4 min
4. Air blow-off or 5-10 sec rinse.....	
5. First fix (alkaline) (Table II).....	6 min
6. Wash.....	5 min
7. Bleach.....	5 min
8. Wash.....	2 min
9. Second fix.....	5 min
10. Wash.....	10 min
11. Dry.....	

5% sodium chloride solution. Figure 7 shows the increased swelling of a film of the borated yellow synthetic binder in tap water. It will be noted that a considerable induction period is required due to the effectiveness of the borate cross-linkages, but after ten minutes the tap water gives rise to a pronounced swelling, not observed in the salt solution. The "salt effect" is also evident when non-borated polymer films are considered. In this case, essentially no induction period is required and the effect is observed immediately. This is clearly seen in Figure 8 which compares the degree of lateral swelling of films of non-borated yellow synthetic binder in tap water versus their swelling in 5% sodium chloride. It can be seen that the swelling not only takes place less rapidly in the salt solution, but also reaches a much lower final equilibrium value. The cyan and magenta color-forming binders exhibit a similar inhibition of swelling by salt solutions.

In conclusion, this paper has attempted (1) to characterize the swelling behavior of films of synthetic color-forming polymers in water and processing solutions, (2)

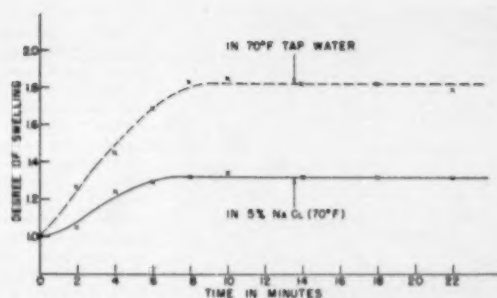


Fig. 8. Effect of salt on swelling of unsupported films of yellow color-forming binders of non-borated polymer.

to describe means for control of swelling, and (3) to apply such controls to permit higher temperature processing of multi-layer films containing these polymers.

Acknowledgment

The authors gratefully acknowledge the technical assistance and advice of their colleagues, Dr. C. W. Bemiss, Dr. A. T. Hallowell and Dr. J. P. Weiss of the Photo Products Department, E. I. du Pont de Nemours & Co.

References

- (1) A. B. Jennings, W. A. Stanton and J. P. Weiss, "Synthetic Color-Forming Binders for Photographic Emulsions," *Jour. SMPTE*, Vol. 55, pp. 455-476, November 1950.
- (2) D. M. McQueen and D. W. Woodward, "Synthetic Color-Forming Photographic Colloids," *J. Am. Chem. Soc.* 73, 4930-34 (1951).
- (3) J. Böeseken and N. Vermaas, "On the Composition of Acid Boric Acid-Diol Compounds," *J. Phys. Chem.*, Vol. 35, pp. 1477-89, 1931.

A CAMERA STAND FOR CINE-PHOTOMICROGRAPHY

Edward H. Bloch* and Alvar Nordstrom

TO RECORD with some degree of facility motion pictures of the microscopic circulation of blood in internal organs transilluminated with the quartz rod, a special camera stand was designed. The camera stand had to have a gross range of motion four to six feet horizontally from its center, an equal range of vertical motion, and three or more feet of lateral motion. A universal range of motion of the camera platform was desired with positive micrometric positioning in the vertical and horizontal planes. This camera platform was designed to accommodate cameras and equipment up to 50 pounds in weight. All movements, gross and micrometric, were required to be made with minimum effort and time since

the camera had to be removable from the field of operation prior to use, then swung into position, the field composed through the beam splitter of the camera, the microscope refocused, and the field photographed. All the operations had to be possible within a period of one to two minutes in case the alignment of the microscope with the internal organs of the anesthetized living subject had to be readjusted so that the rapid changes in the microscopic physiology or pathology could be recorded.

The various requirements listed above were accomplished by erecting a 75 inch tubular steel column (A in figures 1-3) having an outside diameter of 3.75 inches onto a modified "triangular" base of $\frac{5}{8}$ inch boiler plate measuring 42 × 37.5 × 12 inches. This plate (B) was mounted on three free rolling ball bearing casters (C) each wheel measuring 4 inches in diameter and each capable of sustaining a 300 pound load. The wheels of the

* Western Reserve University, Department of Anatomy, Cleveland, Ohio. Received 6 January 1953. This technical development was supported in part by a grant from the Life Insurance Fund. The work was done during the tenure of an Established Investigatorship of the American Heart Association.

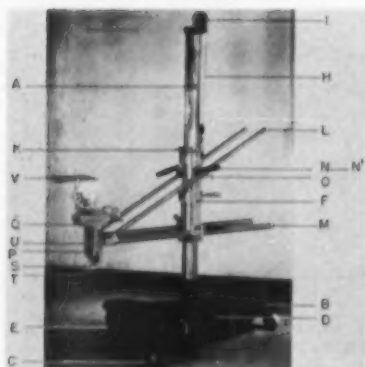


Fig. 1. A main column, B triangular base, C caster, D handle of locking mechanism, E locking pin, H cable for lead counterweight, I wheel of counterweight mechanism, K lock for movable carriage, F movable carriage, L, M shafts, N, N' friction lock and handle for shaft, O check lock, P, Q slides, S wheel for moving slide, T eccentric handle on wheel, U lock.

"tripod" were locked by one motion of an eccentric shaft (D) which depressed a steel bar (E') underneath the base driving three rubber-tipped metal shafts (E) against the floor.

A steel carriage (F) 22.5 inches in length, one inch thick, with an internal diameter of 3.753 and an outside diameter of 6.0 inches was mounted on the vertical column. Movement between the carriage and column occurred through six tool steel roller bearings (G). Three bearings were mounted on each end of the carriage with an eccentric screw for the adjustment of the bearings to insure a snug fit between the bearings (carriage) and the column. Movement of the carriage was controlled by a 300 pound lead counterweight sunk into the lumen of the column. A $\frac{3}{16}$ inch steel cable (H) moving over a 4.25 inch wheel (I) connected the carriage with the counterweight. The counterweight was calculated to balance the carriage (F), shafts (L and M), slides (P and Q), the camera head (V) and 50 pounds of camera. Movement of the carriage was further controlled by two locks, one of which was a leather friction lock (J) while the other was a split circular clamp (K) located at the upper end of the carriage. The tension of this clamp (K) was adjustable either to act as a friction lock, to permit unrestricted movement, or to prevent movement entirely.

Four tubular stainless steel bars (L and M) extended the camera platform to any desired position up to four and one-half feet from the central column. The two upper tubular shafts (L) measured 49 inches in length, while the lower two measured 45.5 inches (M). The outer diameters of the upper and lower shafts respectively were $1\frac{5}{16}$ and 1 inch, with wall thicknesses of $\frac{1}{4}$ and $\frac{3}{16}$ inches.

Movement of these shafts was accomplished by sliding them through friction clamps (N) which were made from cold rolled steel and had a bearing surface of 3 inches. Tension of these clamps was attained by rotating a threaded shaft, eccentrically placed, and which was actuated through a large handle (N') pressing the two steel lips of the clamp together. Each of these clamps was threaded into the carriage in such a way that by extending either the upper or lower shafts it was possible to tilt the unit carrying the camera head either forward, by lengthening the upper shafts, or backward, by lengthening the lower shafts. This rotation of the clamps per-

mitted additional range of movement of the camera head vertically by approximately a foot at the limit of range of movement of the carriage. In extending or shortening the shafts small friction clamps (O) were placed on each shaft. When a change in length of the shafts was desired the clamps were moved into the desired new position, locked, the handles of the large friction clamps turned releasing the shaft permitting them to slide into the desired position. The small check clamps were necessary to prevent the combined weight of the camera head plus shafts from sliding too far or too quickly when adjustment was made.

Lateral rotation of the carriage, approximately 30 degrees from center, was possible without undue lateral tension on the steel cable. Thus the carriage and shafts permitted a considerable degree of gross movement and especially rapid movement in the lateral and vertical planes with some degree of ease.

Positive micrometric movement of the camera was obtained by two aluminum planes (P and Q) attached to the shafts through a 10×1.75 inch bar of aluminum (Q'). Each slide was 8 inches in length $\frac{5}{16}$ inches wide and $\frac{3}{4}$ inch thick made from S-24 aluminum.

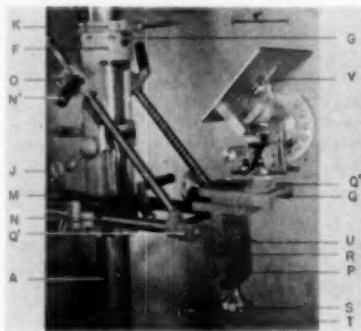


Fig. 2. A main column, F movable carriage, J handle of friction lock, K main lock, M shaft, N friction lock for shaft, M, N' handle of friction lock, O check lock, G roller main bearing, V table of Saltzman tripod head, Q' pedestal, Q slide, Q' aluminum bar, U lock for slide, P vertical slide, S, T wheel and handle for slide, R adjustment.

Slack in the slides was adjusted through type 302 stainless steel gibs. Motion of the slides (4 inches) was made through a threaded shaft having 12 threads to the inch. An aluminum wheel (S) $3\frac{1}{4}$ inches in diameter with an eccentric handle (T) mounted on the rim controlled the movement. The slides could be locked into position by an eccentric stainless steel lock (U).

On the upper plate of the horizontal slide an aluminum pedestal was mounted (Q') into which there was sunk the shaft of a Saltzman tripod head. Movement of this

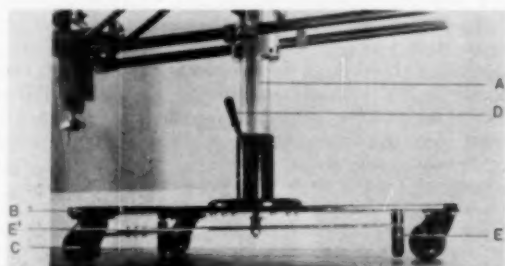


Fig. 3. A main column, B base, C caster, D handle of locking mechanism, E locking pin, E' steel bar.

tripod head was through a worm-gear semi-circular wheel, and friction bearings—all movements being through Cartesian coordinates resulting in nearly universal motion.

The camera stand may be considered as being composed of two separate units one each for gross and micrometric motion. Gross motion is accomplished by the main body of the camera stand which is composed of the central column, the carriage with its extension shafts, and the base. These units give the necessary rigidity to the stand and range of motion. The extension shafts permit placement of the camera into the field of operation without the main body of the camera stand encroaching into the field. Gross vertical positioning of the camera can be quickly accomplished through movement of the carriage on the central column. After roughly positioning the camera it can then be swung out of the field of operation by rotation of the carriage through its shafts. To prevent the camera stand from moving during the subse-

quent operations one simple downward thrust of the eccentric shaft locks the wheels.

The slides comprise the second unit which permit precise micrometric positioning of the camera quickly and without drift in the vertical and horizontal planes. It is these units which give considerable flexibility to the camera stand. Further compositioning of the field is accomplished by rotating and tilting the head as the field is observed through the beam splitter of the camera. When the microscope has to be adjusted, it is only necessary to move the horizontal slide backward, or the vertical slide upward, and push the camera laterally and completely out of the field. Further, since all motions can be made independently of each other, any adjustment can be readily made without disturbing the others.

Finally, as the unit is rugged in construction and rigid, it has been possible to manipulate cameras weighing as much as fifty pounds with considerable ease and without vibration.

SOME CONSIDERATIONS OF RESOLUTION, SHARPNESS, AND PICTURE QUALITY IN TECHNICAL PHOTOGRAPHY

Duncan E. Macdonald*

ABSTRACT

In technical photography, and especially in aerial photography, the capacity of the photographic system to yield information is held to be a measure of its quality. It is postulated that the capacity to yield information is governed by the extent to which symbols can be detected, because gross recognition of different objects depends on such detections. Following up past work which has indicated that detection probability is a function of recorded contrast, contrast thresholds have been determined for various systems. At contrast levels above these thresholds it is possible to detect symbols in the object space through use of the system, whereas no detection is possible at lower than threshold contrast levels. Since the shape, spacing, and size of symbols vary within any one aerial photograph, the contrast threshold should be at a minimum over the weighted range of symbols to be considered. For the sake of simplicity, only the relation of size of symbols to the problem of recognition is considered in this paper. The performance of a system over the entire range of symbols that may have to be explored can be evaluated by determining the maximum area above the appropriate contrast threshold curve. On the other hand, resolution numbers which, as is shown, are unrelated to the probability of detection, and sharpness values are considered to define the optimum conditions for only one size of symbol.

Experiments with a well corrected lens tend to substantiate the above reasoning, since for such a lens the focal settings which yield peak probability of detection vary with symbol size in the same manner as the focal setting for minimum contrast threshold, i.e., maximum contrast. However, it was found that this correlation does not hold for a lens which has considerable residual spherical aberration.

TECHNICAL PHOTOGRAPHY is employed to secure information. Therefore the performance of technical photography is measured by the ability of the photographic system to convey or reveal the desired information. This must relate to the capacity of the system to carry information. Since the nature of the information may vary from one type of investigation to another, it becomes necessary to consider the nature of the message source as

well as the purpose of the technical mission in any quality evaluation.

Take as an example direct astronomical photography. If one may neglect objects in the solar system and such things as nebulosity, nebulae, etc., the message consists solely of bright points on a uniformly dark field. It is clear that if a study is made of close double stars, the ability of the system to render discernable two points in proximity may be considered a measure of performance. This method of measuring performance may be used to evaluate and compare different systems. Such an evaluation was carried out by Dawes¹ and it has led directly to the present resolution testing of optical instruments.

However, if the problem is a search for faint stars or a count of faint stars, then the question arises whether one should be more concerned with the ability of the

* Boston University Physical Research Laboratories, 700 Commonwealth Avenue, Boston 15, Massachusetts. Presented at the PSA National Convention in New York, N. Y., 15 August 1952. Received 3 October 1952.

The research reported in this paper was made possible through support extended the Boston University Optical Research Laboratory by the USAF under Contract No. AF33(038)-15615 (Photographic Reconnaissance Laboratory, Wright Air Development Center). D.E.M.



Fig. 1. Typical astronomical and aerial photographic messages, illustrating the difference in degrees of complexity.

system to differentiate between stars in proximity or with its ability to pack a high percentage of the energy from a point source into a small image point.*

It so happens that probably equal importance should be given both of these requirements in the type of astronomical work cited.

In aerial photography, as in other fields of technical photography, a message source is provided which is coded in silver clumps to be carried back to some point for study. However, in aerial photography one overriding requirement prevails, namely, that the maximum amount of information be secured. Figure 1 shows clearly that the nature of the typical message is far more complex in aerial photography than in the case of astronomy. Instead of bright points on a uniform background, we have a wide distribution of shapes and sizes of objects at different exposure levels. There is no uniformity of background for indeed there is no "background." One might ask if the problem is one of separation of fine details in close proximity, or that of spotting a point in a relatively large field, or the problem of detecting slight tonal changes over relatively large areas. Clearly, these are all involved in analyzing aerial photographs and one might question whether these problems are compatible. That is, if the system were optimized for one particular function, would it necessarily hold that the other function are optimized also?

In review, briefly, an aerial photograph is studied by an interpreter who extracts the message through identification of buildings, vehicles, geologic features, stand heights and stand densities in the case of forestry, etc. In each such case of obtaining information from photographs, the interpreter needs a certain number of detectable symbols on the photograph. It appears correct to consider detection only, since the problem of recognition in photographic interpretation is merely a higher order detection. For example, a gross recognition may be achieved through the detection of the presence of substructure, through the detection of texture characteristics, through the detection of characteristics of detail groupings, or through the detection of a characteristic surface contour.

* Hopkins² has studied in detail the energy distribution in point images, and in the report on his work, "Measurements of the Energy Distribution in Optical Images," presented at the recent National Bureau of Standards Symposium on Optical Image Evaluation, he describes in detail the implications of this "packing fraction."

EXPLANATION OF TERMINOLOGY

Excerpts from a letter to the Editor by Dr. Macdonald in reply to questions on terminology.

"I dislike to see the obvious trend toward a merger of concepts between technical photography (in the sense of a communication system) and the field of communication, i.e., electronics, delayed by semantic difficulty. Photographically we are behind at this point, and I think it is very much in order that we follow along with the established terminology.

"In the field of communication engineering, messages are composed of numbers of *symbols*, and we concern ourselves with the *capacity* of the channel or of the system for carrying *symbols*. Back in 1950, while writing a Laboratory Technical Note (Reference 5), I participated in several long discussions with Dr. Cheatham and Dr. Kohlenberg, our communication engineers, on this semantic problem of *detail* versus *symbol*, and the outcome of that discussion was that *symbol* was the correct term to apply and that we use *symbols* to determine the *capacity* of the system for carrying information—not its capability, but its capacity.

"The term *detail* expresses the concept of minute points; *symbol* represents an abstract term conveying the concept of an element. A *detail* implies an existence, a component of an existing item; a *symbol* is a more flexible term in that it implies a representation of an existing element or merely an abstract representation.

"The term 'background,' as I am using it, does not imply *background* in the pictorial sense. By 'background,' I am assuming the d-c level of the signal. On this basis, any photograph has an average background but, again, as in communication theory a d-c signal does not reveal information; it is only the a-c components, i.e., random or transient responses superimposed on the d-c level, which reveal information."

Previous statistical analyses³ made of commercially usable and nonusable aerial photographs have revealed no significant differences between these two groups in the normalized frequency distribution of edge distances. However, a marked difference is observed in the distribu-

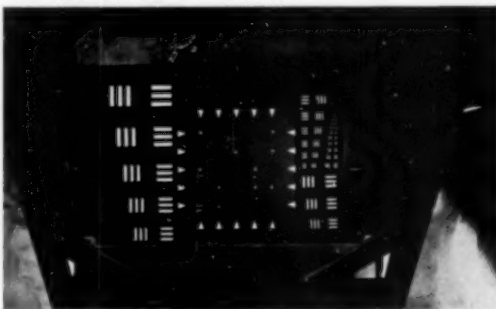


Fig. 2. The target array as seen in the mirror, showing a typical detection pattern at a setting for 100 per cent detection probability.

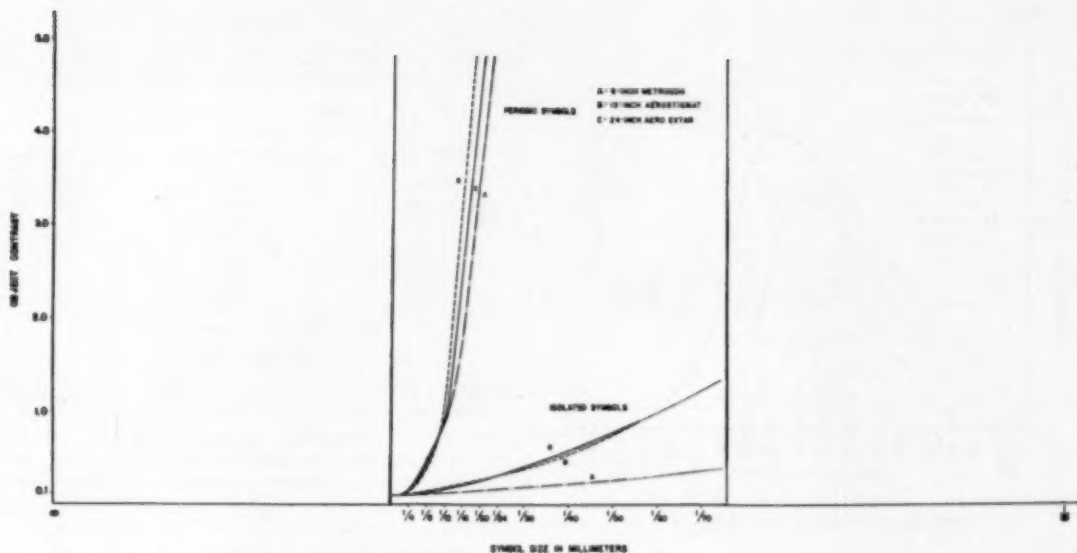


Fig. 3a. Required object contrast as a function of symbol size for periodic and isolated displays.

tion of brightness differences across edges. These results are interpreted as implying that the significant difference between a usable and nonusable photograph is not so much a matter of resolution as of contrast reduction. This concept of contrast reduction is explained in the classic work of Schade⁴.

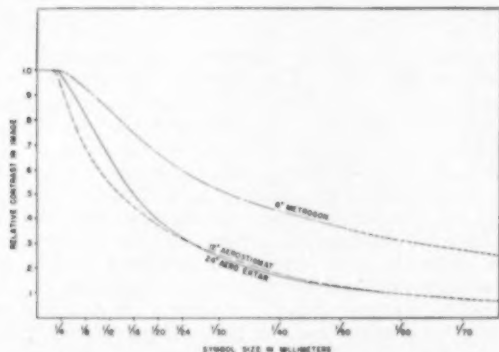


Fig. 3b. Contrast reduction as a function of detail size.

In an approach to this problem of photographic quality our laboratory has investigated the ability of the average observer to detect the presence of basic object forms recorded on various photographic materials. These forms, consisting of squares and circles of the same areas, have been photographed at different scales and recorded at different contrasts and at different resolution levels. It has been previously found and reported⁵ that the detection of a symbol depends only on the contrast as presented to the interpreter and that detection is insensitive to the resolution⁶ at which this contrast is presented.

A second phase of this work has been concerned with the resolution-contrast-scale parameters necessary to

provide differentiation between squares and circles. It has been found that the resolution limit sharply defines the minimum size of symbol that can be recognized. Above this limit the differentiations are performed so long as the contrast is above the detection threshold. The latter observation has led to the previously expressed view that, in general, recognition is a higher order detection.

The Test Method

To assess the probability of detecting symbols, a target array was employed, consisting primarily of a square, uniformly grey background with ten objects, arranged in five rows and five columns, located at random in this 25-position matrix (Figure 2). Photographs taken of this target array are given constant exposure, processed to gamma 1.0 (+0.1, -0.0) and evaluated by a trained and experienced group of analysts. The analysis procedure requires that the observer indicate the ten most probable matrix positions that are occupied by an object on any given photograph. By means of this forced discrimination the guess factor is taken into full consideration. The analysts have shown a high degree of consistency over the past four years on well spaced, repeated trials of test photographs. The probable error of a determination is a function of the probability of detection and reaches zero at 100 per cent probability. The group works at about 3.4 per cent probable error at the 90 per cent probability mark and at about 10 per cent probable error at the 60 per cent probability mark.

The presentation of multiple space choice introduces a search factor. Because of this factor, the results do not represent the true psycho-physical detection thresholds, but some higher characteristic. It is believed, however, that search is contained in the problem confronting the photographic interpreter in his work sequence and, therefore, the particular experimental approach employed

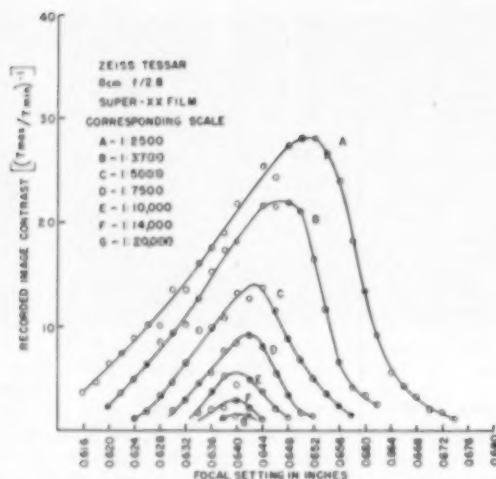


Fig. 4. Image contrast as a function of focal setting with detail size as a parameter.

here provides a reliable and perhaps more representative criterion than would the true threshold.

Throughout the work the dimensions have been scaled for convenience such that the fundamental object is a one-foot (or unit) cube. Simulated aerial photographic scales over a range from 1:2500 to 1:20,000 have been explored in determining the detectability and recognizability of the one-foot cube. No generality is lost by this scaling of the test object. It is only necessary to observe in any such transformation that the ratio of the grain size to the detail image size is held constant. It is thus possible to translate these results to any desired object dimension by applying the same factor to both the object dimension and photographic scale.

The results obtained in this study led to a concept of a detail universe⁷. This universe is represented by Figure 3a which treats of discrete isolated symbols distributed at random over all contrasts and over all linear dimensions, such that for any area $(\Delta x)(\Delta c)$ we first assume the same number of symbols. (In this illustration two important dimensions are neglected, exposure level and form factor.) In aerial photography the system is tuned to explore any preselected range of sizes by selecting flight altitude. On one hand, it is limited by its angular coverage, the other dimension limit being some measure of resolution. Contrast reduction of the system as a function of the detail size has been measured frequently in the laboratory. (Figure 3b presents such data for three lenses.) From such data it is possible to define the contrast threshold characteristic of the photographic system, $\Psi(x)$, in Figure 3a.

The difference in threshold characteristics for isolated symbols as opposed to periodic symbols such as occur in resolution targets is noteworthy for this emphasizes the difference in performance characteristics of the system for these two types of symbols. From the information gathered in this laboratory and from the work of Carman and Carruthers⁸, we learn that the distribution of symbols in contrast is skewed very heavily towards the low-contrast end. Thus, the importance of lowering the

Table I

OPTIMUM FOCUS FOR MAXIMUM LINE CONTRAST AND MAXIMUM PROBABILITY OF OBJECT DETECTION

8-cm Zeiss Tessar f/2.8 lens
Focal Setting In Inches Assessed by

Symbol Scale	Maximum Contrast	Detectability
20,000	0.640	0.671
14,000	.641	.672
10,000	.643	.673
7,500	.644	.675
5,000	.645	
3,700	.648	
2,500	.651	

Table II

OPTIMUM FOCUS FOR MAXIMUM LINE CONTRAST AND MAXIMUM PROBABILITY OF OBJECT DETECTION

12-inch Aero Ektar f/2.5 lens
Focal Setting in Inches Assessed by

Symbol Scale	Maximum Contrast	Detectability
20,000	0.372	0.484
14,000	.367	.492
10,000	.367	.491
7,500	.368	.489
5,000	.369	.486
3,700	.370	.484
2,500	.375	.481

weighted contrast threshold over the significant object sizes becomes evident.

It has been long established that the focal settings for minimum flare and maximum resolution do not necessarily coincide. In fact, reference has been made to the work of Hansen⁹ who reported an experiment which indicates that observers select photographs in terms of sharpness as related to minimum flare rather than to maximum resolution. Consequently, this work has been extended, and most recently an objective definition of photographic sharpness has been presented by Higgins and Jones¹⁰ as a result of their experimentation.

It is observed, however, that any judgment of sharpness must consider the conditions of viewing. The unaided eye can detect density fluctuations corresponding to about 4.25 lines per millimeter on Super-XX emulsion. Any judgment of photographic sharpness on this material made with unaided vision cannot consider the rendition of any finer detail. Moreover, it has been observed that comparative sharpness judgments may reverse themselves as viewing magnifications are changed. In such work as aerial photography, where the observer desires to extract information from the largest to the very limit of the smallest recorded dimensions, the problem becomes somewhat involved.

The hypothesis that the volume, or the area of the detail universe that lies above the contrast detection threshold of the system shown in Figure 3b, can be taken to measure the information capacity of the system was subjected to test. Users of aerial photographs generally specify maximum resolution while various laboratories have extended this to specify minimum flare, or minimum flare for the expected minimum symbol size. While all of these requirements have particular merits, they all consider a discrete point for examination and none takes into account the weight of the distribution of symbol

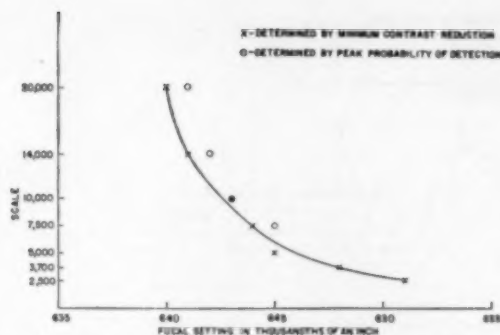


Fig. 5. Illustrating the shift in focus with scale (image size), as determined by two methods described by the author.

sizes over the range of symbols admissible by the system. As has been stated previously¹¹, the present study sought the minimum flare (minimum contrast reduction) for the particular size of image which is of primary interest. If several different sizes are of equal interest, it then becomes necessary to achieve a weighted minimum flare over these sizes.

For any given lens, a shift in focal setting will generally result in an intersection in the contrast characteristics for the two focal settings. The focal setting for maximum resolution gives minimum contrast reduction for the image size corresponding to the resolution limit. Another setting will give minimum contrast reduction for some other size of image. To substantiate the hypothesis it is then necessary to establish that the point of minimum contrast reduction (maximum contrast rendition) coincides with the position of maximum detectability.

An f/2.8 Zeiss Tessar 80mm lens was selected for test. A test object consisting of isolated single white lines on a dark field was collimated and photographs taken through focus. The target dimensions were so selected that the line widths were imaged at 1/2500, 1/3700, 1/5000, 1/7500, 1/10,000, 1/14,000, and 1/20,000 of a foot. The resulting photographs were then measured with a microphotometer and image contrast was plotted against focal settings with detail size as a parameter. Typical plots are shown in Figure 4.

The same lens was then employed to photograph the target array. From these data was plotted the probability of detecting a given symbol size as a function of focal setting. To determine the best focus for object detection, a graphical integration was performed over the area lying above the zone which gave 80 per cent, or greater, probability of detection of the symbol. The mean focal setting for this value is employed. The results are shown in Table I. At scales 1:5,000 and larger, 100 per cent detectability was achieved throughout such a wide range of focal settings that no attempt was made to push the data further. Thus, a focal setting was determined for each scale which provided peak contrast rendition (i.e., minimum contrast reduction) as well as a focal setting that provided the peak probability of detecting the corresponding symbol size.

Inasmuch as the detection experiments were made with a finite object distance, a calculated correction factor of 0.030 inch must be applied to the focal setting.

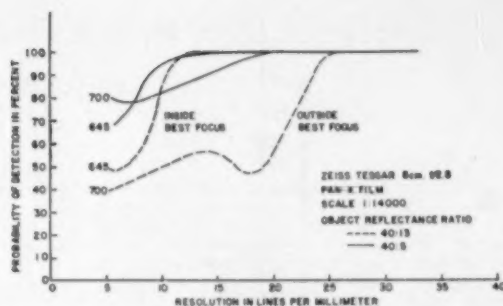


Fig. 6. Probability of detection as a function of resolution.

With this factor applied, the results are plotted in Figure 5 and the correlation between shift in focal settings for the contrast rendition and for the criterion of detectability of detail is readily apparent.

Resolution and Detectability

It is of particular interest to see the lack of relationship between resolution and detectability. This is clearly shown in Figure 6 where the resolution data have been read from the same frame on which the detection data were assessed. One notices, for two object contrasts studied, the different values of resolution at which 100 per cent probability is achieved and the different rates at which the probability of detection moves toward the 100 per cent value with resolution as one approaches the optimum focal setting from inside focus or from outside focus. From these results it can be inferred that the shape of the contrast threshold curve in the detail universe is important and that it is correct to measure or interpret the performance of the system in terms of the area of the space above the threshold curve.

On the other hand, one must be cautious because it is found that other results are obtained by use of a lens having a large amount of aberration. For example, the 12-inch f/2.5 Aero Ektar lens has residual spherical aberrations such that, if one runs through focus on axis, a high probability of detection of isolated symbols is still possible long after the contrast in the line image has dropped below its peak and the resolution has ap-

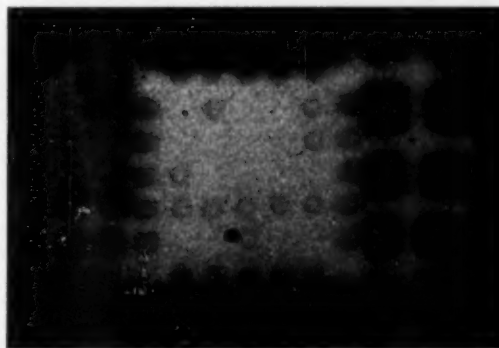
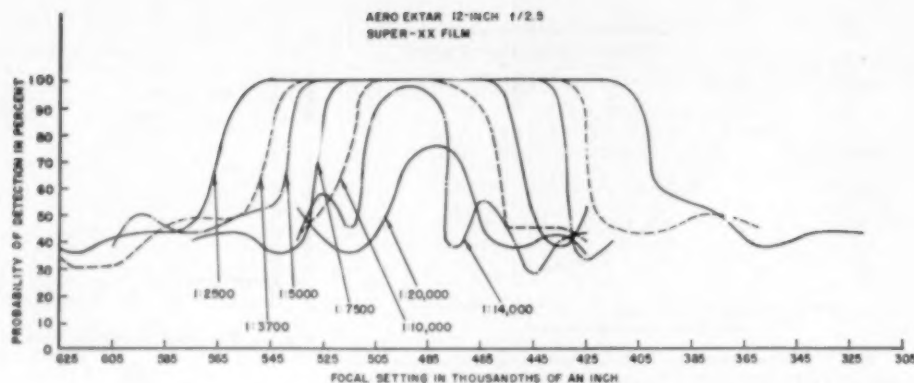


Fig. 7. The target array under conditions of spurious resolution.

Fig. 8. Probability of detection of unit squares as a function of focal setting with scale as a parameter.



proached zero, and, in fact, a high degree of spurious resolution has set in (Figure 7). One reason is the presence of the ring-shaped energy distribution which gives, in effect, an image at a much larger scale.

The results of detection experiments with the 12-inch $f/2.5$ Aero Ektar lens are shown in Figure 8. That there is a shift in focal setting to provide peak detectability at various scales is evident. It is also evident, as might be expected, that as one goes to larger scales there is a larger range of focal setting along the axis which provides peak detectability. The results of experiments with the $f/2.5$ Aero Ektar lens are shown in Table II. The correction factor to be applied to the focal setting as determined by detectability is 0.115 inch. Obviously the curves fold in opposite directions and there is no relationship between peak contrast in the line image and peak detectability of squares.

Summary and Conclusions

In the case of technical photography, the information capacity of the photographic system is held to be a measure of its quality. It is then assumed that the detection of symbols relates to this capacity on the ground that the gross recognitions are built up through these detections. On the basis of past work, which has indicated that the detection probability is a function of recorded contrast, contrast thresholds have been determined for various systems. Symbols in the object space at contrasts above these thresholds may be detected through use of the system whereas those objects at lower contrasts are not detected. The old argument relative to minimum flare-maximum resolution settings manifests itself in this suggestion through changes in shape and position of the threshold characteristic as the focal setting is varied. On the grounds that the shape, spacing, and size of symbols vary within any one aerial photograph, it is further suggested that the threshold must be at a minimum over the weighted range of symbols that are to be considered. For simplification, only size has been considered here. To treat the threshold characteristic and to maximize the area over it (or to minimize the area under it) weights the performance of the system over the entire range of symbols which it may be called upon to explore, whereas resolution numbers, which are shown to be unrelated to probability of detection, and

sharpness measures are held to optimize conditions for only one size of symbol. Experiments on a well corrected lens tend to substantiate the above arguments, as the focal setting for achieving peak probability of detection varies with symbol size in the same way as does the focal setting for minimum contrast threshold (i. e., maximum contrast). On the other hand, it is found that with the presence of a considerable degree of residual spherical aberration these arguments do not hold. This dichotomy necessitates additional work which is now in progress.

Acknowledgments

Many have contributed. Particular credit is due to Mr. Donald McBrien and Mr. William Attaya for their considerable effort in carrying out all the photographic aspects, to our analysis group headed by Miss Rose Thomas who have patiently and carefully interpreted the many photographs, and to Mr. John Watson for his continual advice, comments, and constructive criticisms.

References

1. W. R. Dawes, *Memoirs of The Royal Astronomical Society of London*, Vol. 35, p. 158 (1865-66).
2. R. E. Hopkins, "Measurements of the Energy Distribution in Optical Images," from the report of The National Bureau of Standards Symposium on Optical Image Evaluation, October 1951, *Image Quality of Optical Systems*. National Bureau of Standards. In Press.
3. D. E. Macdonald, "Quality Aspects of the Aerial Photographic System," *ibid*.
4. O. H. Schade, "Electro-Optical Characteristics of Television Systems" (in four parts), *RCA Review*, Vol. 9, pp. 5-37, 245-286, 490-530, 653-686 (1948).
5. D. E. Macdonald, "Criteria for Detection and Recognition of Photographic Detail, Part I—Resolution, Scale and Contrast Conditions for Isolated Detail," B.U.O.R.L. Technical Note No. 69, July 10, 1950. Also, "Calibration of Survey Cameras and Lens Testing," *Photogrammetric Engineering*, Vol. 17, pp. 383-389 (1951).
6. *Op. Cit.*, Macdonald, "Quality Aspects of The Aerial Photographic System."
7. *Ibid*.
8. P. D. Carman and R. A. F. Carruthers, "Brightneses of Fine Detail in Air Photography," *J. Opt. Soc. Am.*, Vol. 41, p. 305 (1951).
9. G. Hansen, *Zeiss Nachrichten*, Vol. 6, pp. 129-137 (1942).
10. G. C. Higgins and L. A. Jones, "The Nature and Evaluation of the Sharpness of Photographic Images," *J. Soc. Motion Picture Engrs.*, Vol. 58, pp. 277-290 (1952).
11. *Op. Cit.*, Macdonald, "Criteria for Detection and Recognition of Photographic Detail," Part I, and "Calibration of Survey Cameras and Lens Testing."

THE SHARPNESS OF PHOTOGRAPHIC IMAGES

G. C. Higgins and L. A. Jones*

ABSTRACT

The ability of a photographic material to produce pictures having good definition is commonly referred to as its sharpness, which is a subjective concept. It is suggested that the objective correlate of sharpness be termed acutance. It is shown that acutance computed from a microdensitometer trace across an abrupt boundary between a light and a dark area in the developed image correlates with sharpness evaluated by direct observation. The acutance values are computed from the microdensitometer trace as the triple product of: (a) the average gradient computed in the usual way, (b) the average gradient computed at equal increments of density instead of distance, and (c) the difference in density between the light and the dark area in the image. It is shown that, contrary to the generally accepted belief, resolving power does not correlate well with sharpness judgments and in some cases is even misleading.

AN IMPORTANT FEATURE of a photographic print is the sharpness with which details are reproduced. As every photographer knows, the sharpness of a print depends upon such factors as the quality of the camera lens and the characteristics of the photographic materials. Sometimes the photographer uses all his skill to obtain a needle-sharp reproduction, as when a complicated mechanism is to be illustrated by a photomechanical process, while at other times, he may equip his camera or enlarger with a diffusing screen to reduce the sharpness for artistic effect.

Sharpness is a subjective concept, since it is the impression received by an observer when he views a print. By viewing a series of prints, an observer can arrange them in their order of sharpness. Furthermore, when several observers arrange the same series of prints in their order of sharpness, numerical values of sharpness can be assigned to the prints by reducing the data by statistical procedures. This method of obtaining quantitative values of sharpness is difficult to apply in practice, and could be avoided if an objective method were available for obtaining values that would correlate with sharpness. The obvious usefulness of an objective measurement which will predict sharpness of pictures made on a photographic material led to an investigation

into the nature of sharpness and the physical characteristics of a picture that determine the impression of sharpness when the picture is viewed.

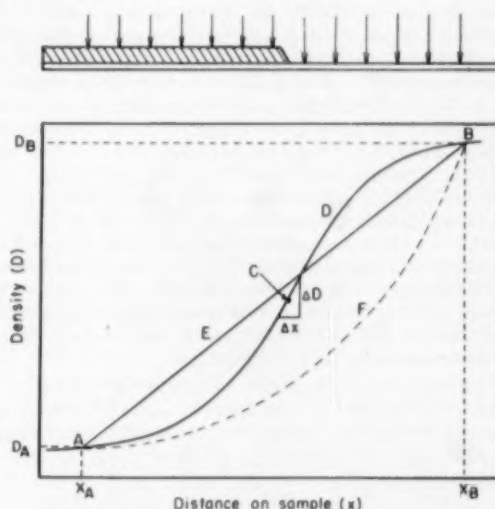


Fig. 1. Schematic diagram representing a knife-edge exposure and the corresponding microdensitometer trace, *D*, across the developed image. The straight line, *E*, and the hypothetical dotted curve, *F*, between points *A* and *B* represent traces having the same average gradient as curve *D*.

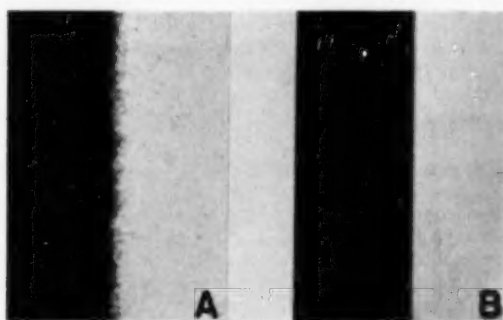


Fig. 2. Photomicrographs of knife-edge images (300X). A, high-speed emulsion of low acutance; B, high-contrast emulsion of high acutance.

* Research Laboratories, Eastman Kodak Co., Rochester, New York. The material presented in this paper is substantially the same as that contained in "Nature and Evaluation of Image Sharpness," by G. C. Higgins and L. A. Jones, *Jour. SMPTE*, Vol. 58, p. 277, 1952. Received 6 December, 1952.

The sharpness of a picture is normally judged by examining the manner in which the density in the image varies across an abrupt boundary between a light and a dark area. When photographic materials are exposed while partially shielded by a knife edge in contact with them, as shown schematically at the top of Figure 1, the photographic images resulting after processing are similar to those shown in Figure 2. These images, when enlarged as in Figure 2, show that the density does not drop abruptly to zero at the former location of the knife edge but that the image encroaches on the area that was shielded during the exposure and has a diffuse boundary. The diffuseness of the edge depends markedly upon the photographic materials. A fine-grained material with low

turbidity will, in general, produce a knife-edge image having a rapid change in density across the boundary, as is shown at B in Figure 2; while a coarse-grained material with high turbidity will produce a knife-edge image in which the density will vary slowly across the boundary, as is shown at A. A microdensitometer trace across the image of a knife edge, like the ones shown in Figure 2, is similar to curve D shown at the bottom of Figure 1. The ordinates of this curve represent density as a function of the distance, x , across the knife-edge image. It will be seen that the density change is not abrupt at the knife edge, but that, instead, the density starts to increase well within the shadow, and, in this particular case, attains its maximum at a point well within the illuminated region.

It seems reasonable to expect that the ability of a material to produce sharp pictures should be related to the variation in density across the image of a knife-edge exposure, since the judgment of sharpness is made primarily by examining the manner in which edges are reproduced in the picture. To carry the study further, it is necessary to introduce the mathematical concept of gradient. Consider the point, C, on curve D in Figure 1. For any small increase in distance, Δx , the density rises by an amount ΔD . The gradient at point C is then defined as the ratio $\Delta D/\Delta x$, and the problem is to determine what characteristic of this gradient is determinative of sharpness. It is clear that, over the course of the curve, the gradient starts at zero, rises gradually to a maximum (Fig. 1 has been drawn in such a way that C is at its maximum), and then gradually diminishes to zero again. One assumption—and one that would lead to a simple method of evaluation—is that the maximum value of the gradient is the feature that determines the sharpness of the image. Unfortunately for this simple hypothesis, Wolfe and Eisen¹ studied a series of prints and showed definitely that it is untrue.

If the eye does not take the maximum gradient as its criterion of sharpness, perhaps it takes the average gradient between two points, such as A on the toe and B on the shoulder. This average gradient, G_x , is, of course, simply the ratio $(D_B - D_A)/(x_B - x_A)$. Wolfe and Eisen also tested this hypothesis but found no simple relation between sharpness and the average gradient of the microdensitometer curve, regardless of the criterion upon which the limiting points A and B were selected. A little consideration will show that this result is not surprising. Both the straight line, E, and the broken line, F, passing through A and B in Figure 1 have the same average gradient as curve D. On the other hand, it is highly unlikely that three materials whose edge gradients are represented by these three curves would give rise to the same sensation of sharpness. Evidently, further knowledge of the behavior of the eye is required.

It is well known that, under usual conditions of illumination, equal differences in density between two areas give rise to equal sensations of brightness difference. That is, the brightness difference between a density of 0.5 and 1.0 in a print appears to be approximately the same as the brightness difference between a density of 1.0 and 1.5 in the same print. The receptors in the eye that evaluate these brightness differences are the cones, thousands of which examine the image formed on the retina whenever a photograph is viewed. When we

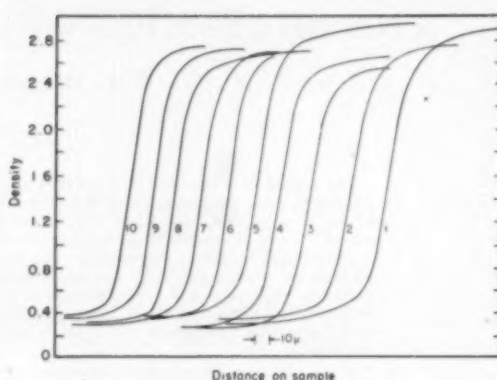


Fig. 3. Microdensitometer traces across the images in the positive as printed from knife-edge images on ten different negative materials.

look fixedly at the edge of the photographic image discussed above, our eyes are continually moving back and forth, and the cones actually scan the image some 50 to 100 times per second, even when we think that the eye is perfectly motionless. The eye thus determines the sharpness of an image in much the same manner that we determine the texture of a piece of cloth by running our fingers over it. Recent evidence indicates that the response transmitted from the cones to the brain depends upon the suddenness with which the illumination falling on the cones varies as the image is scanned.² Since, as noted, the sensation of brightness differences is related to density differences, the response of the cones is proportional to $\Delta D/\Delta t$, where ΔD is the difference in density between two areas in the picture which are scanned by the cones in the time Δt . The temporal gradient $\Delta D/\Delta t$ can be divided into two components, $\Delta D/\Delta x$ and $\Delta x/\Delta t$, since

$$\frac{\Delta D}{\Delta t} = \frac{\Delta D}{\Delta x} \frac{\Delta x}{\Delta t} \quad (1)$$

Now $\Delta x/\Delta t$ is the velocity with which the cones scan the image on the retina. The other component, $\Delta D/\Delta x$, such as the one shown at C in Figure 1, is clearly the gradient in the image. While C here represents the maximum gradient, the sensation of sharpness must be determined by the appearance of the entire edge; a meaningful evaluation of the trace must take into account the values of the gradients $\Delta D/\Delta x$ at all points.

In a sense, the average gradient G_x takes all these values into account, because it can be computed by a method that involves summing up all values of $\Delta D/\Delta x$ between the points A and B at equal increments of distance x . It seems logical that this average gradient should have some effect upon an observer's impression of sharpness, but it has been pointed out above that it alone is not the determining factor, probably because it fails to take the shape of the curve into account. Another type of average gradient that does take the shape into account can be computed by a method that involves summing up $\Delta D/\Delta x$ for equal increments of density D instead of equal increments of distance x . In addition to taking the shape of the curve into account, this procedure has the added merit of recognizing that the eye

sees equal differences in density as equal differences in brightness. This type of average density, which can be expressed as \bar{G}_D , can be computed for curve D by measuring the gradient $\Delta D/\Delta x$ at points on the curve for which $D = 0.1, 0.2, 0.3$, etc., up to $D = 2.0$ or whatever value of D corresponds to the limiting point B. These gradients are then added together and divided by the number of them (20 in this case) to obtain \bar{G}_D .

Assuming that both types of average are equally effective in determining the sensation of sharpness, we may multiply them together and test their product as an objective correlate of sharpness. Here a fortunate circumstance intervenes. It is often easier to obtain the values of gradient at equal increments of x than at equal increments of D , and it is not much more difficult to compute the average of the squares of the individual gradients than the average of the gradients themselves. Now it can be shown mathematically³ that the average of these squares taken at equal increments of x is

$$\bar{G}_x^2 = \bar{G}_x \cdot \bar{G}_D. \quad (2)$$

This means that the desired product can be obtained directly by measuring the individual gradients, $\Delta D/\Delta x$, at equal increments of x , squaring them, adding the squares, and dividing by the number of increments that were measured.

When the gradients are averaged as just described, a certain minimum gradient must be selected as the criterion for the initial point, A, in the toe, and the final point, B, in the shoulder. It seems reasonable to select as the limiting gradient the lowest gradient that is capable of producing a response in the eye. Investigations in physiological optics indicate that for the light-adapted eye, this threshold gradient is approximately 0.005 in density per micron. Experience may show that this value should be modified, but for the lack of a better criterion, it was used in the present study.

Total Density Scale Influences

In addition to the gradient characteristics of the edge, it is conceivable that the total density scale, DS , between the dense and the clear parts of the negative may influence an observer's judgment of sharpness. Suppose, for example, that two edges had density gradients that could be represented by curve D in Figure 1, but that the density scale, $DS = D_{\max} - D_{\min}$, was 2.0 for the first and only 0.5 for the second. (Since the average slope is by hypothesis the same for both edges, the quantity $x_{\max} - x_{\min}$ must also be four times as great for the first as it is for the second.) Although definite results have not been obtained on this point, it seems reasonable to assume that an observer would consider the first edge to be sharper than the second edge. Whether he would consider the first edge to be four times as sharp as the second may legitimately be questioned, but the authors tentatively propose that DS be introduced directly as a factor. It is proposed that the objective correlate of sharpness be termed *acutance*, and that an acutance defined as $\bar{G}_x^2 \cdot DS$ be examined as an objective correlate of sharpness. The whole question as to whether DS should be introduced can, of course, be avoided by comparing images in which DS is the same, and this was done in all the cases described.

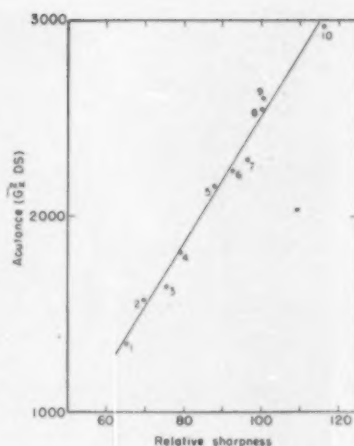


Fig. 4. Acutance plotted as a function of sharpness. The points represent values for ten negative materials and correspond to the traces of Figure 3.

To determine the validity of acutance as an objective criterion of sharpness, we must return to actual prints viewed by observers. Wolfe and Eisen made a positive transparency from each of ten different negative materials which had been used to photograph the same scene. These transparencies were matched, as nearly as possible, from the standpoint of tone reproduction. They were then ranked for sharpness by twenty observers. Three different methods of ranking were employed, but since they all gave substantially the same results, only one will be described. This particular method consisted in presenting to an observer two of the ten transparencies at a time. The observer was instructed to decide whether the transparencies were equally sharp, or, if not, which was the sharper. Each of the ten transparencies was thus compared with the other nine, one at a time. From these data, it was possible to apply statistical methods for deriving scale values that gave quantitative significance to the results. While the absolute value of the number assigned to each material had no significance by itself, the relative values of the numbers represented quantitative differences in sharpness. On this basis, Wolfe and Eisen were able to say not only that materials 4, 5, and 6, for example, ranked in that order of sharpness, but that their quantitative sharpness rankings, on a relative scale, were given by the numbers 79, 88, and 92. That is, they could say not only that one material was sharper than the other, but also how much sharper as compared with the other materials being investigated.

Knife-edge images were printed on all ten negative materials, and these images were in turn printed to make positive transparencies in the same manner as the picture negatives had been printed. Microdensitometer traces across these knife-edge images in the positives are shown in Figure 3. While the differences between the traces appear to be quite small, the differences between the values of acutance can be calculated from these traces with considerable certainty. The values of acutance of all ten materials are plotted in Figure 4 as ordinates, and the corresponding values of relative sharpness, as determined by judging the pictures, are plotted as abscissas. It is evident that all materials are ranked in the same order on the acutance scale as they are on the sharpness scale and, moreover, they are spaced approxi-

Fig. 5. The least sharp (A) and the sharpest (B) pictures made from negatives on ten different materials. They correspond to traces 1 and 10, respectively, of Figures 3 and 4.



mately the same on both scales. The coefficient of correlation between the sharpness values and the acutance values is 0.994. The sensitivity of this method of evaluating sharpness is shown by Figure 5, in which A is a print made from material 1, which is the least sharp, while B is a print made from material 10, which is the sharpest. Although all the judges ranked B above A, the difference is so small that it may not be evident in the photomechanical reproduction of the pictures. On the other hand, Figure 4 shows that the acutance of these materials is 2970 and 1350, respectively, a ratio of more than two to one.

It was stated earlier that the maximum slope of the curve of edge gradient does not correlate with sharpness. This is well shown by materials 3 and 4, whose curves in Figure 3 have essentially the same maximum slope. Nevertheless, the observers found that prints from material 4 were sharper than prints from material 3. Examining the curves more closely, one sees that curve 3 rounds off at the shoulder somewhat more than curve 4, and that it also has a slightly lower density scale. These factors are reflected in the difference in sharpness exhibited by Figure 4.

Sharpness and Resolving Power

For many years it was the practice in the photographic field to report values of maximum resolving power. Resolving power is measured by photographing a series of line gratings and determining the number of equal-width lines and spaces which are just resolvable when the developed image is examined visually under adequate magnification. While these values were intended specifically as a measure of the ability of the film to record fine detail, such as double stars or fine parallel lines, it has been generally assumed that they were a measure of the ability of the material to produce sharp pictures. Experience has shown, however, that resolving power

as usually measured does not correlate well with sharpness judgments and, in some cases, may be even misleading. The lack of correlation between resolving power and sharpness is strikingly shown by Figure 6. The same negative was printed on two experimental positive materials to give the best matched tone reproduction possible. The positive material used in printing picture A has a maximum resolving power in excess of 230 lines per millimeter, while the positive material used in printing picture B has a maximum resolving power of only 130 lines per millimeter. Even though the material used in making print B has a very much lower resolving power, the picture is clearly much sharper than print A. When the pictures shown in Figure 6 were made, knife-edge images were also printed on the two positive materials. Microdensitometer traces across these images are shown in Figure 7, and the difference between the two traces is readily apparent. Trace A, representing the less sharp material, has a very low slope and a long toe and shoulder, while trace B, representing the sharper material, has a relatively high slope and an abrupt toe and shoulder. The value of acutance for the sharp material having the low resolving power is 12,210, while the value of acutance for the unsharp material having the high resolving power is only 2,800.

The reason for the relatively high resolving power of the unsharp material is evident from Figure 8. This figure shows microdensitometer traces across the image of clear lines 6 microns wide when exposed directly on the two positive materials. The unsharp material, A, has a very narrow "throat" but a long, sweeping toe, while the sharp material, B, has a much more abrupt toe but an appreciably wider throat. When narrow lines are exposed adjacent to each other, the combined image consists of two density peaks with a slight valley between. The steeper the individual density curves, the closer the images can approach each other and still leave a perceptible valley. Thus material A, with the nar-

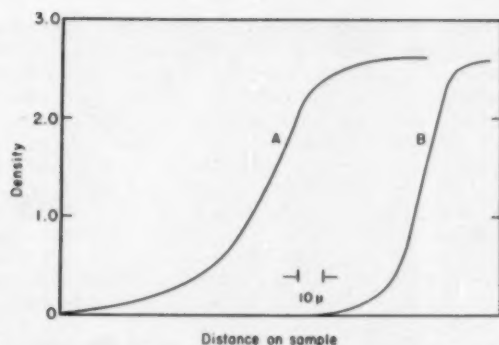


Fig. 7. Microdensitometer traces across knife-edge images printed onto the two positive materials used for the pictures of Figure 6.

rower throat, exhibits a higher resolving power than does material B, despite its more sweeping toe and consequently lower acutance.

The same technique that is applicable to the sharpness characteristics of photographic materials should also be applicable to the sharpness characteristics of lenses. Theoretically, it is the aerial image formed by a lens that should be studied, but this is extremely difficult from an experimental standpoint, and since the end result is usually a photographic reproduction, photographic methods can give much useful information.

Wolfe and Eisen examined a 12-inch lens, designed for photography, by photographing the same picture repeatedly, the photographic material being placed at different distances from the lens for the successive exposures. The negatives were then printed on photographic paper and the resulting prints were judged for sharpness. A standard resolving power test chart was also photographed repeatedly under the conditions used in making the picture negatives. Since resolving power varies greatly with exposure, an exposure series was made for each position of the film and the maximum value at each

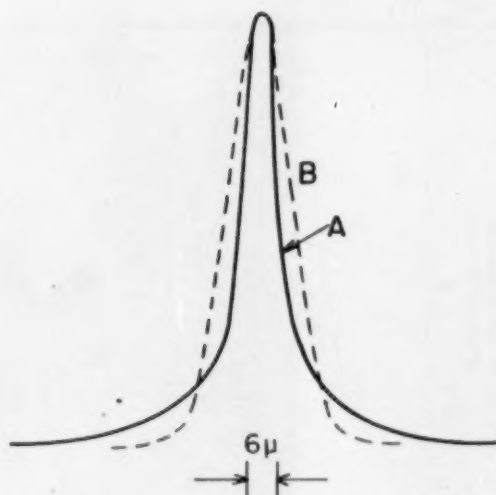


Fig. 8. Microdensitometer traces across the images of a 6-micron line on the two positive materials used for the pictures of Figure 6.

position, regardless of the exposure, was determined. The results are shown in Figure 9, where maximum resolving power and relative picture sharpness are plotted as functions of the position of the film in the camera measured from an arbitrary point. The lack of correspondence between sharpness and resolving power is strikingly exhibited in this figure; not only are there two maxima of resolving power and only one of sharpness, but also there is a difference of fully one millimeter between the position on the axis for the highest maximum resolving power and the position for the maximum sharpness.

This independence of resolving power and sharpness can be elucidated by Figure 10, which shows two images

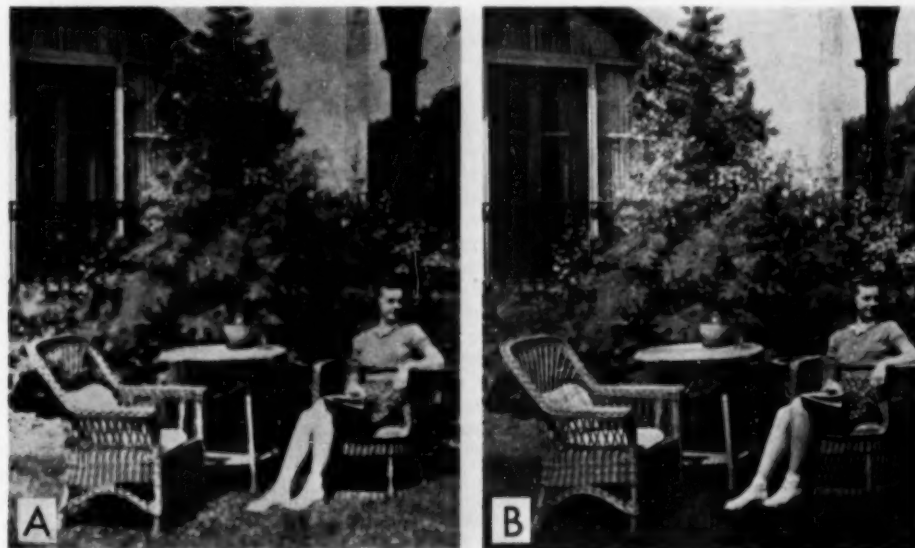


Fig. 6. Prints from the same negative on two experimental positive materials. The resolving power of material A is 230 lines per millimeter, while that of material B is 130 lines per millimeter.

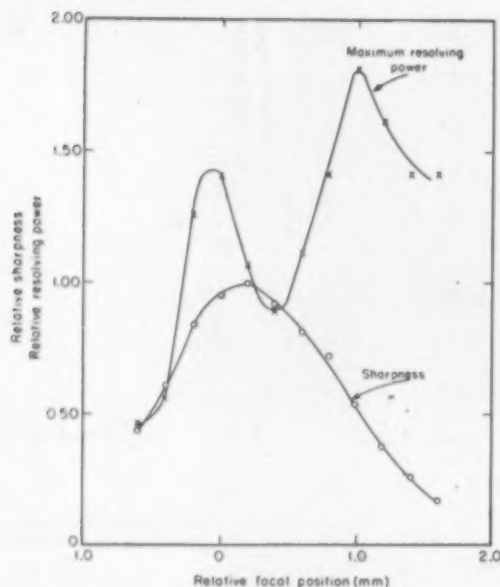


Fig. 9. Relative maximum resolving power and relative sharpness of pictures plotted as a function of the relative distance from lens to film when the negatives were made.

of a point source made by the lens. The image at A was formed at the position for maximum resolving power. It consists of a small central disk surrounded by very weak rings. (The pattern is similar to the well-known Airy diffraction pattern, except that spherical aberration has increased the relative illuminance in the outermost ring.) Since the rings are too faint to be recorded under ordinary conditions, the important feature is the central disk, and despite the degradation arising from the limitations of photomechanical reproduction, the unsharpness of the outer portion of this disk is unmistakable. On the other hand, the image made at the position of maximum sharpness and shown in B, although considerably larger than the central disk in image A, has a much sharper boundary.

Knife-edge images were made at the same positions of the film as were used for recording the images shown in Figure 10 and microdensitometer traces across these

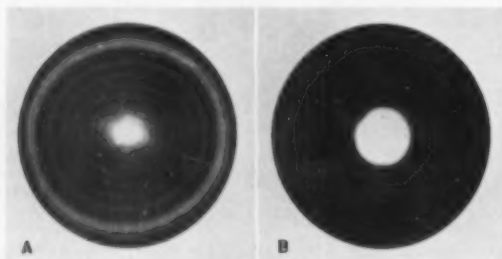


Fig. 10. Greatly magnified photographic reproductions of the image of a point source as formed by a lens. The position of the plate along the axis was such as to give (A) maximum resolving power and (B) maximum sharpness.

knife-edge images are shown in Figure 11. The values of acutance as computed from these two traces are 165 for trace A and 620 for trace B. A glance at the figure is sufficient to show why the acutance of the former is less than that of the latter, but the reason for the superior resolution of the former requires closer study. The gradient of trace B is fairly constant over the major portion of the trace, but that of curve A, although low over most of the trace, becomes very high in a short region just below the shoulder. The difference between these traces is much like the difference between the two traces shown in Figure 8, and the reason adduced there for the better resolution of the less sharp material can be applied to the present case.

The significance of this study can be seen in a practical way from Figure 12. Photograph A is a print made from the negative that was exposed at the position for which the resolving power of the lens was a maximum, while photograph B was made from the negative exposed at the position for maximum sharpness. The difference between the characteristics of the two photographs is unmistakable.

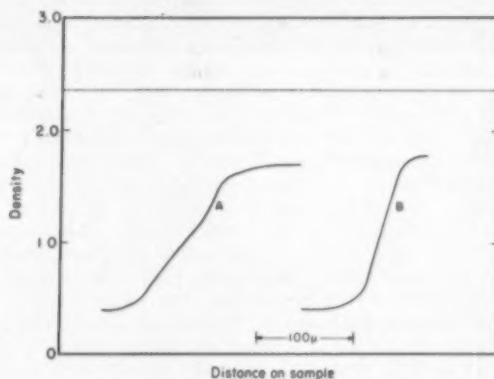


Fig. 11. Microdensitometer traces of knife-edge images formed by a lens on a photographic material. The plate was placed at the position of (A) maximum resolving power and (B) maximum sharpness, as for Figure 10.

Although this experiment shows that resolving power as usually measured cannot be used to predict with certainty the ability of a photographic material or a lens to produce sharp pictures, resolving power is nonetheless an important property of photographic materials and lenses. When the eye views a scene 14 inches away, it can resolve a maximum of about 10 black and white lines per millimeter in the scene under the best conditions. When the same eye views a photograph, it feels unsatisfied if details of this order of magnitude are not present, and there are indications that the presence of even smaller details is still more satisfying. Thus, the resolving power of the lens and film must be sufficient to satisfy the limits set by the eye for the conditions under which the photograph will be viewed.

Summary

To sum up, all the results obtained to date indicate that acutance measured as $G^2 \lambda \cdot DS$ can be used to predict the



Fig. 12. Photographic reproduction of a scene for which the negatives were made at the position of (A) maximum resolving power and (B) maximum sharpness. These correspond to the respective traces of Figure 11.

sharpness of pictures made with different photographic materials. These results also indicate that this acutance concept is useful in evaluating the sharpness characteristics of an image produced by a lens. However, the density difference, DS , across the knife-edge images was essentially the same for all the samples investigated. The results cited, therefore, do not indicate whether DS should be introduced into the formula for acutance, or, if so, whether it should be introduced as a weighted function. Many more experiments are required before a comprehensive expression for acutance that will hold under all conditions can be evolved, and still more before the conditions of manufacture, exposure, and proc-

essing of photographic materials can be evaluated for their effect on acutance. Even then, the whole field of the interrelation between sharpness, graininess, and resolving power, insofar as they affect our impression of picture quality, will remain to be explored.

References

1. Robert N. Wolfe and Fred C. Eisen, *J. Opt. Soc. Amer.*, in press.
2. Loyd A. Jones and George C. Higgins, "Photographic Granularity and Graininess: III. Some Characteristics of the Visual System of Importance in the Evaluation of Graininess and Granularity," *J. Opt. Soc. Amer.*, Vol. 37, p. 217, 1947.
3. Loyd A. Jones, "The Contrast of Photographic Printing Paper," *J. Frank. Inst.*, Vol. 203, p. 111, 1927. The derivation cited is on pp. 136-7.

PHOTOGRAPHY IN A GENERAL HOSPITAL

Leonard A. Julin*

ABSTRACT

In the popular mind, photography in a general hospital means "before and after" pictures of patients. There are many other applications, depending on the size of the hospital staff and the nature of its activities. Various applications of photography in a general hospital are explained: staff conferences, case histories, laboratory reports, progress records, scientific papers, exhibits, instruction, and public relations. A description of some special photographic equipment and technique is included.

PHOTOGRAPHY CAN SERVE in many ways in a general hospital, but the extent to which it is applied depends a great deal on the size of the hospital and the scope of its activities. In a small private hospital, the only photography may consist of a few pictures taken by one of the doctors using his own camera. At the other extreme may be a large hospital, perhaps associated with

a medical school, which has a staff of professional photographers and is equipped with a variety of photographic devices. The term "devices" is used because equipment differing greatly from ordinary cameras frequently is used.

In general, photography is used for recording, for reporting, and for teaching. The basic demand for photography in a hospital is for recording the appearance of a patient, or of a pathologic lesion or specimen, such as a tumor. The next need is for making lantern slides or photographic prints to be used in reporting the case at a staff meeting or in a medical journal. For teach-

*Section of Photography, Mayo Clinic, Rochester, Minnesota. Presented at the PSA National Convention, New York, N. Y., 12 August 1952 as part of the Technical Division Symposium on Photography in Medicine and Biology. Received 4 December 1952.

ing, these same pictures may be utilized, but usually it is necessary to have additional photographs for specific teaching situations.

The doctor may want a photograph of the patient to illustrate a rare disease or unusual condition, or, on the contrary, perhaps the picture is made to show that the patient appears to be in normal health while actually he has a serious illness. A collection of selected photographs can show the medical student a greater number of similar pathologic conditions than he probably would encounter in a lifetime of medical practice, and thus will aid him in recognizing a disease.

The patient who has undergone a plastic operation on her face may forget her former appearance or may have dreamed of much greater improvement in her appearance and consequently may sue the doctor for damages. In such situations, a preoperative photograph of the patient is an invaluable record for the doctor.

Sometimes, a patient desires a photograph showing physical disability so he can use it when claiming compensation insurance. Some government and welfare agencies require that photographs be made of patients that they refer to a hospital for treatment. In some cases of disease the change for better or for worse may take place so slowly that photographs provide the best record of progress.

In the laboratory, a surgical specimen may be photographed before it is cut for further study grossly and microscopically. Photomicrographs are a common part of the pathologist's record. Likewise, the bacteriologist may utilize photography to make a permanent record of colonies growing on culture plates.

Motion pictures are ideal for recording disorders or limitations of movement and for demonstrating various technical procedures. Color motion pictures are especially suited for illustrating surgical operations and for recording rapid changes in color such as the flushing or blanching that may follow the administration of a drug. Action that is too rapid or brief for careful observation can be studied from slow-motion pictures. In some cases of disease, the patient's speech is affected, and this has been recorded on sound motion pictures. Time-lapse motion pictures made through a microscope can speed



Fig. 1. A photograph of this patient's appearance is far more effective than a verbal description.

up the apparent motion of living tissue cells or parasites that normally move too slowly for observation.

It is common practice for the members of a hospital staff to hold meetings at which they discuss various cases, report on postmortem findings, and hear the results of research projects. At these meetings, it is customary to use lantern slides that have been made from photographs, from typewritten tables and case histories, and from hand-drawn graphs. Also on the program may be motion picture films that have been borrowed from medical film libraries.

At the larger meetings held by medical societies, it is customary to use similar projection material and also to display exhibits that contain enlarged prints or transparencies. Such exhibits also form part of a medical museum.

Motion and still pictures can supplement instructions given to patients. For example, the arthritic patient may need massage and other forms of home treatment that can be given by a member of his family after receiving instructions. For this purpose, motion pictures are especially good for demonstrating the technic of massage and manipulation of joints. The patient with diabetes,

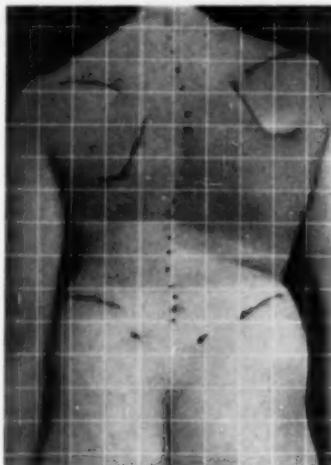


Fig. 2. Spinal curvature is demonstrated by the black marks which have been applied by the physician. The photographic negative is printed in register with a ruled grid. Similar photographs made subsequently provide a record of improvement.

and members of his family, must learn about the disease and how to control it. Here color photography is well suited for showing the color changes that occur in the solutions that are used when testing for the presence of sugar.

Photography can be used to improve the morale of a patient. For example, a patient who is improving very slowly from some disability may become quite discouraged until he sees motion pictures of his earlier condition which reveal that he has improved much more than he realized. Some hospitalized patients, such as those who are recovering from the effects of poliomyelitis, have been provided with a photographic darkroom where they can practice photography as a hobby. Motion picture programs of an entertaining nature also have been provided for such patients. Incidentally, the hospital photographer usually has charge of projection equipment.



Fig. 3. Blood vessels that were almost invisible are very conspicuous in this photograph which was made by infrared light on infrared sensitive film.

Photography Aids Medical Research

A considerable amount of photography in a hospital may be associated with medical research. For example, a large number of photographs (color, black-and-white, still and motion-picture) were made when studying the effects of penicillin and of cortisone. Photography in medical diagnosis as well as in research frequently requires special equipment, technic and skill.

If photographs of patients are to be used for comparison, it is necessary to have similarity of pose, image size, lighting, background and photographic technic. The patient may be unable to co-operate with the cameraman, but the latter must obtain the best picture possible while remembering that the welfare and comfort of the patient are of the most importance. Frequently, it is necessary to take close-up photographs which require the use of a long bellows extension. A small diaphragm aperture is needed to provide sufficient depth of field, but at the same time the exposure must be short enough to avoid a blurred image due to movement of the subject. For this reason, flash bulbs or gaseous discharge lamps

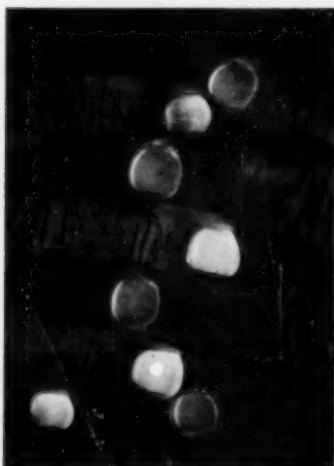


Fig. 4. Ultraviolet "black light" was used when photographing these fluorescing finger nails.

frequently are used as a source of light for exposure. Tungsten lamps may be used for focussing and as fill-in light. Sometimes spotlights are employed to emphasize contour or texture. Basic exposures can be standardized, but the posing, lighting and photographic technic require considerable judgment and skill on the part of the cameraman. For instance, a photograph of a face may be technically perfect, but the plastic surgeon may consider it worthless because the patient's head was turned a fraction of an inch too far. The photograph of a skin lesion that is perfect in the opinion of the dermatologist would not have been so if the photographer had not used ortho film instead of panchromatic, and if he had not used a spotlight to emphasize the texture of the lesion.

Various common cameras can be utilized in medical photography, but the most universal one is a view camera which uses sheet film. Also used are 35mm cameras



Fig. 5. Cross section of an abnormally large spleen. The comparative size of an average normal spleen is outlined with white string.

with extension tubes or bellows. Special cameras may be used for certain purposes, such as photography of the eye, of body cavities and of operations. In addition, there are photographic recording devices that are distinctly unlike the ordinary camera and usually are operated by laboratory technicians rather than by professional photographers.

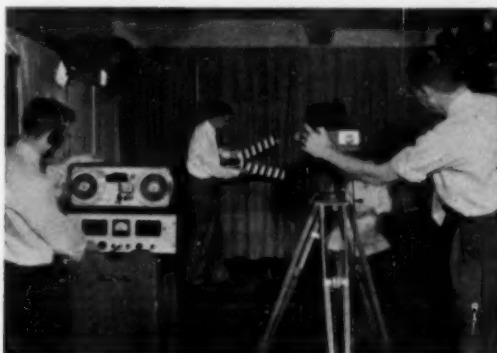


Fig. 6. Making sound motion pictures with a synchronous magnetic tape recorder. Later, the sound is rerecorded on film for printing with the picture.

In photomicrography, the microscope serves as a camera lens. Photomicrographs can be made with a small camera supported over a microscope, but greater flexibility and better results are obtained with special photomicrographic equipment. Frequently, it is necessary to make photographs at a scale of 1:1 or slightly greater, but these photomicrographs are made with short focus lenses rather than with a microscope. The art of photomicrography requires long study and practice, and is only one of the many technical activities of the medical photographer.

Although the making of x-ray pictures involves a photographic process, the work is done by x-ray technicians. However, when a roentgenogram is to be reproduced as a lantern slide or a print, it is given to a photographer for copying by transillumination. The superimposed images on the front and rear surfaces of a radiograph may extend the density range too far for reproduction in a copy. Consequently, it may be necessary to sacrifice some detail in the reproduction. The photographer, therefore, should know what diagnostic detail is important and must be retained.

Photographic copying is an important activity in the hospital. Copies are made of illustrations in text books, of charts, of tabular material, and of drawings and graphs made by the art department. Litho negatives also are made of various printed forms for reproduction by the printing shop. Photographic copying provides a permanent record of material that may fade or change in other ways.

The photocopy process, which permits one to make copies directly on paper instead of film, is used mainly by the administration office and the medical library. Microfilming is utilized when certain records are wanted in small form for compact storage. Similarly, a 16mm recording camera is used to photograph all checks and money orders received by the business office. The autostat is a rapid process that is used in ordinary room light for making reflex copies of correspondence. The Ozalid, rapid daylight duplicating process is used for making contact copies of translucent material, such as manuscripts typed on thin paper, and of shop drawings.

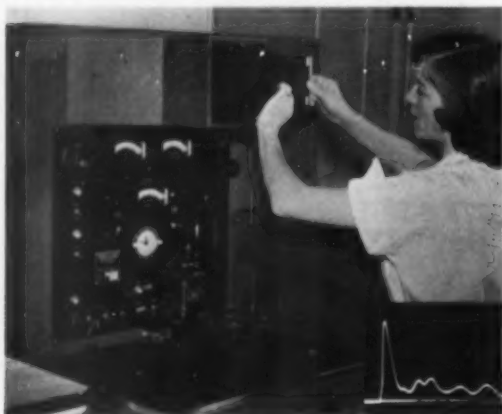


Fig. 7. An electrophoresis camera that can be used for recording diffraction differences in solutions of blood proteins produced the record shown in the insert.



Fig. 9. Kymographic records ranging in size up to 18 inches by 200 feet are processed on a motor driven unit. The records are dried on a drum dryer which has a motor driven take-up spool.

Some of the special photographic technics that are used include infrared photography which is used mainly to record veins and some surface lesions. Ultraviolet rays are used when photographing fluorescence which is seen in certain skin diseases and when fluorescing substances are injected into the body. Polarized light may be used in photomicrography and to eliminate glaring highlights on wet specimens.

The electrocardiographic unit, a device for recording heart beats, usually is operated by a laboratory technician. The recorder uses a roll of light-sensitive paper or 35mm film. As the paper or film moves past an aperture, it is

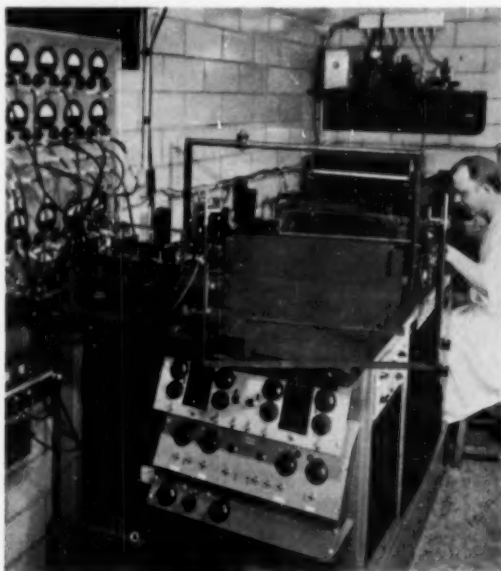


Fig. 8. In the kymographic camera, beams of light controlled by galvanometers are projected onto a moving roll of photographic paper to produce a variety of records.

exposed to a beam of light which is deflected by a galvanometer that is motivated by the activity of the heart.

Oscilloscopes are finding increasing use in medical laboratories, and a variety of recording cameras are available for photographing the pattern on the oscilloscope screen. Another kind of recording device, used in the biochemistry laboratory, is the electrophoresis camera. This contains a light source and a system of lenses and mirrors that produces a photographic record of diffraction differences in solutions of blood proteins.

Laboratory personnel working with or near radioactive material may be exposed to harmful amounts of the powerful rays. In order to guard against excessive exposure, the workers wear badges that contain film and identification data. The films are developed at selected intervals to determine if there is any fogging from excessive exposure to radioactivity.

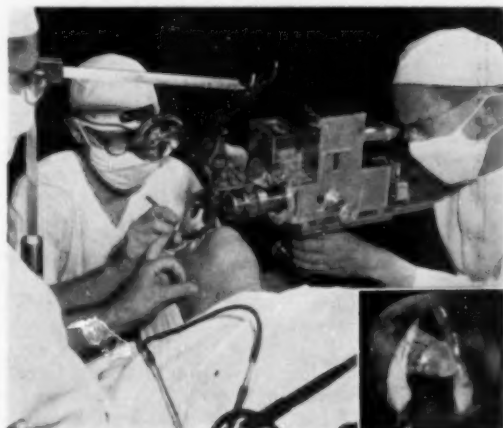


Fig. 10. Making motion pictures of the vocal cords. The use of a small mirror near the mouth of the patient permits the camera to record what the surgeon is doing. The inserted photograph, which was made from a 16 mm. film, shows a growth on the vocal cords.

Special cameras have been built for photographing within body cavities. One such unit is an endoscopic camera for making motion pictures of the larynx or vocal cords. The retinal camera is designed for photographing the inside of the eye, and usually is operated by the ophthalmologist.

For photography of surgical operations, one of two general methods is used. In the first method, a camera having a lens of long focal length is used at a safe distance from the operative field. In the second method, a camera having a lens of normal or short focal length is used near the surgical field, and precautions are taken



Fig. 11. A sterile housing containing a fixed-focus, battery-driven camera provides an easy way for a surgeon to take photographs during an operation.

to avoid contaminating the operative area. Camera housings that can be sterilized have been described in the literature.^{1,2}

Patients who are to have an operation performed on the heart undergo a number of laboratory tests. One of these is catheterization of the heart, during which a catheter is inserted into chambers of the heart. Various recording devices that are attached to the patient lead to a kymographic camera in another room, where beams of light are deflected by galvanometers onto a moving roll of photographic paper. The roll of exposed paper, which may be as large as 18 inches by 175 feet in size, is processed in a modified unit that originally was built for developing aerial photographic film.

In addition to doing his processing, the medical photographer must be well versed in basic photography and be able to make excellent photographs of a wide variety of subjects, and to work with an extensive assortment of photographic equipment, techniques and materials, often under difficult conditions. He must be familiar with medical terminology and know how to produce a picture that is "just what the doctor ordered," and he must get it the first time—he can't ask for "just one more" when he is photographing the removal of a gallbladder or the delivery of a baby.

References

1. Ingraham, F. D., and Cobb, C. A., Jr.: Simple Method of Making Photographic Records Under Sterile Conditions. *J. Neurosurg.*, Vol. 4, pp. 293-297 (May) 1947.
2. Julin, L. A.: A Semiautomatic Aseptic Surgical Camera. *J. Biological Photog. A.*, Vol. 18, pp. 163-167 (Nov.) 1950.

Density Measurements up to 9.0

At a meeting of the R.P.S. Scientific and Technical Group held January 29, 1953, Dr. E. H. Belcher discussed the usefulness of the photomultiplier tube for scintillation counting and for photographic densitometry. By cooling the tube with liquid nitrogen to suppress the background "noise," Dr. Belcher measured densities up to 9 in connection with studies

on the Callier coefficients of images produced by x- and gamma radiation.

Dr. G. Spiegler and Mr. B. E. Keane used the photomultiplier tube at room temperatures in a simple instrument to measure diffuse densities up to 6.0. A constant current was maintained through the multiplier, as the incident light intensity varied, by altering the voltages supplied to the dynodes.

G. I. P. LEVENSON

INFLUENCE OF OXYGEN AND MOISTURE ON THE HERSCHEL EFFECT

W. Vanselow, R. F. Quirk, and T. H. James*

ABSTRACT

An investigation was undertaken to determine the influence of oxygen on the Herschel effect on emulsions which had been conditioned and subsequently exposed in a gaseous atmosphere of controlled humidity. Comparisons were made between the Herschel effect obtained in oxygen and in nitrogen atmospheres at relative humidities of approximately 0%, 20%, and 52%. Tests were made on a pure silver bromide primitive emulsion, an iodobromide primitive emulsion, a pure silver bromide emulsion chemically sensitized to give a material of moderate speed and coated both with and without desensitizer, two similar emulsions containing 1 mole % and 3 mole % silver iodide, likewise coated both with and without desensitizer, and a commercial motion-picture positive emulsion. The Herschel effect increases in going from 0 to 20% relative humidity with all emulsions when the exposures are made in an atmosphere of nitrogen, and with the emulsions which do not contain desensitizer when the exposures are made in oxygen. The magnitude of the Herschel effect in the primitive emulsions and the pure silver bromide emulsion shows little or no dependence on oxygen; the effect is larger in the presence of oxygen when the motion-picture positive emulsion or the chemically sensitized iodobromide emulsion containing 1% iodide is used. The Herschel effect in the pure silver bromide emulsion desensitized by pinakryptol yellow is enhanced by the presence of oxygen at 0% relative humidity, but is independent of oxygen at 20%. Both oxygen and humidity have a marked effect upon the infrared speed of the chemically sensitized bromide emulsion. The density obtained by infrared exposure in nitrogen at 20% humidity is only about one-fourth that obtained at 0%; the density obtained at 0% humidity in oxygen is only about one-fourth that obtained in nitrogen. Similar, but smaller, effects were observed with the iodobromide emulsions.

SEVERAL REFERENCES to the influence of moisture and of the nature of the surrounding atmosphere on the Herschel effect have appeared in the literature. Narbutt¹ obtained a more pronounced Herschel effect on a wet paper emulsion than on a dry one. Blau² obtained less Herschel effect on paper emulsions when the paper was contained in a vessel evacuated to 6 mm during the red-light exposure than when the exposure was made at atmospheric pressure. She found that the difference was even more pronounced when the emulsion had been desensitized by a dye. Vnukova³ found that the Herschel effect was enhanced by oxygen and moisture, whereas the effect practically vanished in atmospheres of nitrogen and carbon dioxide. Bäckström⁴ found that the Herschel effect was much smaller on an emulsion from which the surrounding air had been evacuated and replaced by nitrogen than on a control emulsion which was exposed in air. Blau, Vnukova, and Bäckström assume that oxygen plays an important role in the mechanism of the Herschel effect. On the other hand, Thurston and Blair⁵ did not find any significant influence of the surrounding gaseous medium on the Herschel effect with the emulsions they tested.

The discordance between the results of Blau, Vnukova, and Bäckström on the one hand, and of Thurston and Blair on the other may arise from the fact that they used different emulsions. However, the experimental technique employed by each is open to criticism. The evacuation procedure used by Blau and Bäckström undoubtedly caused some change in the moisture content of the film, and, according to the results of Narbutt and Vnukova, this in itself would alter the magnitude of the Herschel effect. The change in moisture content is probably at least partly responsible for the change which Blau and

Bäckström attribute to a decrease in oxygen pressure. Thurston and Blair likewise take no account of possible changes in moisture content, and there is no evidence from their description of their experimental procedure that the gaseous atmospheres used were at the same relative humidity. It is not clear that Vnukova's experimental data support her contention that the Herschel effect practically vanishes in atmospheres of nitrogen and carbon dioxide. Table 1 and Figure 2 of her paper, which give a comparison of the results obtained in atmospheres of air, oxygen, nitrogen, and hydrogen, show that the apparent sensitivity of the emulsion to red light in the absence of initial white-light exposure is considerably greater in nitrogen than in air, and slightly greater in air than in oxygen. The densities obtained with red-light exposure but no previous white-light exposure are: 0.24 in oxygen, 0.26 in air, 0.54 in nitrogen, and 0.60 in hydrogen, compared with a basic fog density of 0.12 in the absence of any exposure. If the curve representing the Herschel effect in nitrogen is "corrected" for this increase in red-light sensitivity by shifting the curve along the density axis until the point corresponding to no white-light exposure coincides with the corresponding point for the curve representing the Herschel effect in air, the resulting curve for nitrogen shows a Herschel effect only slightly smaller than that in air. In view of the relatively large differences in red-light sensitivity in oxygen and in nitrogen, it is doubtful if any valid conclusion as to the influence of the two gases on the Herschel effect can be drawn from Vnukova's data. She gives no data for carbon dioxide.

The present investigation was undertaken to determine the influence of oxygen on the Herschel effect on emulsions which had been conditioned and subsequently exposed in a gaseous atmosphere of controlled humidity. Comparisons were made between the Herschel effect obtained in oxygen and in nitrogen atmospheres. Three

* Communication No. 1526 from the Kodak Research Laboratories. Received 13 November 1952.

degrees of relative humidity were employed: approximately 0%, 20%, and 52%. In one experiment, tests were also made at 79%. The film samples were conditioned for 16 hours at the desired relative humidity in an apparatus described in a previous publication.⁶ All exposures were made while the film was still in the apparatus. The white-light exposure was for 0.1 second through a step tablet consisting of three bands of neutral-density filters, each 4.5 cm wide, and having densities of 0.26, 0.52, and 1.0. A 250-watt tungsten-filament lamp was used as light source at a distance of 94 cm. The Herschel-effect exposure was of 1 hour's duration, and the light used was from a 500-watt projection-type lamp filtered through one No. 25 and two No. 87 Kodak Wratten filters. The lamp was situated 94 cm from the film. Development was for 4 minutes in Kodak Developer D-16 at 20 C. The control films were given no infrared exposure, but were kept in the apparatus for 1 hour following the white-light exposure before they were removed and developed.

The evacuation technique used by Bäckström⁴ in his investigation of the influence of oxygen on the sensitivity of photographic emulsions was checked by comparing the sensitivity of film which had been treated as follows: (1) control (no treatment), (2) held 24 hours over phosphorus pentoxide, (3) evacuated 24 hours, (4) held 24 hours over phosphorus pentoxide in a nitrogen atmosphere, and (5) evacuated 24 hours over phosphorus pentoxide and then stored 24 hours in nitrogen over phosphorus pentoxide. The last four conditions all yielded the same developed densities within the limit of experimental error, and these were approximately 10% higher than those of the control. The difference is probably a consequence of the change in moisture content. It may be concluded that the 24-hr exhaustion period is not necessary.

Experimental Results

Two primitive* emulsions,⁷ prepared by W. G. Lowe, were tested. These emulsions showed no red sensitivity, and hence the results are free from the complications existing in emulsions where the Herschel-effect exposure can create latent image. Emulsion A is a pure silver bromide, emulsion B an iodobromide emulsion. Table I gives the detailed results obtained with the bromide emulsion, A. The fog densities (no white-light exposure) for the film which has received the infrared exposure, HE, agree within the limit of experimental error with those of the control, C, showing that the Herschel-effect exposure will not form a latent image in this emulsion. The white-light sensitivity of the emulsion drops sharply on changing from 0% relative humidity (R.H.) to 20%. The sensitivity decreases further in going from 20% to 52%. The sensitivity in oxygen is less than in nitrogen at 0% and 20% R.H., but is substantially the same at 52%. The same statements apply throughout to the results obtained with the iodobromide emulsion.

Table II gives the percentage change in density (average) in nitrogen and oxygen brought about by the infrared exposure. The Herschel effect is essentially

* Primitive emulsions are those emulsions having no chemical sensitization, their sensitivity being due to crystal irregularities.

Table I

EFFECT OF OXYGEN AND MOISTURE UPON HERSCHEL EFFECT OF PRIMITIVE EMULSION, A

Relative Humidity (%)	Nitrogen		Oxygen	
	C	HE	C	HE
~0	2.78	2.88	2.38	2.46
	1.88	1.78	1.15	1.12
	0.24	0.29	0.09	0.10
Fog	0.04	0.05	0.05	0.05
20	1.92	1.74	1.48	1.33
	0.84	0.67	0.45	0.32
	0.10	0.09	0.08	0.08
Fog	0.04	0.06	0.04	0.05
52	1.73	1.50	1.73	1.46
	0.67	0.44	0.61	0.32
	0.09	0.06	0.08	0.08
Fog	0.06	0.05	0.05	0.06

Table II

PERCENTAGE LOSS IN DENSITY CAUSED BY HERSCHEL EXPOSURE

Relative Humidity (%)	Primitive Emulsions			
	B		A	
	Iodobromide Nitrogen	Oxygen	Bromide Nitrogen	Oxygen
~0	0	4	-3	-3
20	25	29	10	10
52	20	27	10	15

absent for both emulsions at 0% R.H. The influence of oxygen at the higher R.H. values is small.

The investigation was continued with a pure bromide emulsion which had been chemically sensitized to give a material of moderate speed. Three coatings were made of this emulsion: C, the basic emulsion; D, containing the desensitizer, pinakryptol yellow; and E containing the desensitizer, pinakryptol green. The intensity of the white-light exposure was adjusted by means of neutral densities so that the same range of developable densities was covered with all three emulsions. Table III shows the results obtained in the Herschel-effect experiments. A comparison of the fog values for the control and the infrared exposure of the basic emulsion, C, shows that this emulsion has considerable infrared sensitivity, particularly at 0% R.H. in a nitrogen atmosphere. The sensitivity to infrared is much less in oxygen than in nitrogen at this R.H. The sensitivity to white light, on the other hand, is only slightly less in oxygen than in nitrogen at 0% R.H. At 20% and 52% R.H., the infrared sensitivity is only slightly less in oxygen than in nitrogen, and the white-light sensitivity is even less dependent on the atmosphere. The desensitizers decrease the infrared sensitivity in a nitrogen atmosphere at 0% R.H., eliminate it in an oxygen atmosphere at 0% R.H., and eliminate it in both atmospheres at 20% and 52% R.H.

Experiments also were made with an iodobromide emulsion, F, containing 1 mole percent iodide; the same emulsion coated with pinakryptol yellow desensitizer, G; an iodobromide emulsion containing 3 mole percent iodide, H; and the same emulsion coated with pinakryptol yellow, I. Emulsions F and H show considerable sensitivity to the infrared exposure, but this sensitivity is less dependent upon humidity and oxygen than that

Table III

PURE BROMIDE EMULSIONS
DENSITY VALUES SHOWING EFFECT OF OXYGEN AND MOISTURE UPON HERSCHEL EFFECT

Relative Humidity (%)	Emulsion											
	C AgBr Control				D AgBr + Pinakryptol Yellow				E AgBr + Pinakryptol Green			
	Nitrogen		Oxygen		Nitrogen		Oxygen		Nitrogen		Oxygen	
	C	HE	C	HE	C	HE	C	HE	C	HE	C	HE
~0	1.52	1.40	1.40	1.34	1.80	1.68	1.43	0.64	1.61	1.16	1.09	0.68
	1.19	1.11	1.09	0.99	1.52	1.14	0.85	0.38	1.27	0.83	0.88	0.46
	0.61	0.78	0.57	0.55	0.98	0.48	0.41	0.18	0.76	0.53	0.46	0.23
Fog	0.06	0.37	0.04	0.10	0.04	0.08	0.03	0.04	0.05	0.08	0.03	0.03
20	1.34	1.06	1.32	0.96	1.34	0.52	0.99	0.42	1.16	0.60	1.07	0.45
	0.99	0.79	0.95	0.72	0.88	0.26	0.73	0.18	0.89	0.33	0.81	0.20
	0.48	0.52	0.48	0.45	0.47	0.08	0.38	0.09	0.52	0.13	0.41	0.08
Fog	0.04	0.15	0.04	0.12	0.02	0.02	0.04	0.02	0.02	0.03	0.04	0.03
52	1.46	1.10	1.43	1.07	1.30	0.44	1.05	0.42	1.20	0.60	1.13	0.48
	1.13	0.80	1.08	0.80	0.86	0.23	0.78	0.20	0.95	0.33	0.88	0.20
	0.60	0.57	0.56	0.56	0.47	0.09	0.43	0.09	0.60	0.03	0.46	0.09
Fog	0.04	0.15	0.04	0.12	0.04	0.04	0.03	0.04	0.04	0.03	0.03	0.04

Table IV

PERCENTAGE LOSS IN DENSITY OWING TO HERSCHEL EXPOSURE

Relative Humidity (%)	Emulsion											
	D AgBr with Pinakryptol Yellow				F AgBr + 1 M% AgI				G AgBr + 1 M% AgI with Pinakryptol Yellow			
	C AgBr		Nitrogen		Oxygen		Nitrogen		Oxygen		Nitrogen	
	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen
~0	8	4	7	55	-8	-6	22	60	-12	-4	26	67
20	21	27	61	57	5	-1	62	79	-1	9	75	83
52	25	25	66	60								

Table V

PERCENTAGE LOSS IN DENSITY CAUSED BY HERSCHEL EXPOSURE
(EMULSIONS BATHED IN POTASSIUM BROMIDE)

Relative Humidity (%)	Emulsion											
	D AgBr with Pinakryptol Yellow				F AgBr + 1 M% AgI				G AgBr + 1 M% AgI with Pinakryptol Yellow			
	C AgBr		Nitrogen		Oxygen		Nitrogen		Oxygen		Nitrogen	
	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen	Nitrogen	Oxygen
~0	21	27	17	90	5	13	81	88	11	9	82	88
20	37	26	86	85	30	39	86	80	28	29	86	87
52	35	36	85	78	25	58	84	75	21	43	82	81

of the pure bromide emulsion. The fog densities of the control and the HE-exposed strips of emulsion F are 0.19 and 0.44 at 0% R.H. and 0.18 and 0.40 at 20% R.H. under nitrogen; 0.16 and 0.34 at 0% and 0.10 and 0.28 at 20% under oxygen. The corresponding values for emulsion H are 0.10 and 0.42 at 0%, 0.10 and 0.36 at 20% under nitrogen; 0.11 and 0.36 at 0%, 0.10 and 0.22 at 20% under oxygen. The desensitizer destroys the infrared sensitivity of both emulsions under oxygen but only partially destroys it under nitrogen at 0% R.H. The desensitized emulsions show no infrared sensitivity under either gas at 20% R.H.

The percentage decrease in density caused by the HE exposure is given for each emulsion in Table IV (averaged values). The values given for the emulsions without desensitizer are of little significance because of the high infrared sensitivity of these emulsions. The values for the desensitized emulsions show a marked influence of oxygen on the Herschel effect at 0% R.H., but no influ-

ence of oxygen on the Herschel effect at 20% and 52% for the pure bromide emulsion and only a small influence at 20% for the iodobromide emulsions.

The inherent infrared sensitivity of the emulsions without desensitizer can be reduced to insignificance by bathing the emulsions for 2 minutes in 0.1 M potassium bromide solution and then drying them. The results obtained with the three basic emulsions and with the corresponding emulsions containing pinakryptol yellow following the bromide treatment are given in Table V in terms of the percentage decrease in density caused by the HE exposure. Oxygen exerts little or no influence on the Herschel effect on emulsion C, and exerts a significant effect on emulsion H only at 52% R.H. Oxygen enhances the Herschel effect on emulsion F at all R.H. values, but the influence is marked only at 52%. On the other hand, the influence of oxygen is pronounced at 0% R.H. on the desensitized emulsion, D. With this emulsion at 20% and 52% R.H. and with the other de-

sensitized emulsions at all R.H. values, a very large Herschel effect is observed in nitrogen as well as in oxygen, and the influence of the gas probably is not significant.

Finally, a few tests were made on a commercial motion-picture positive-type emulsion which shows a moderate Herschel effect. The percentage decrease in density produced by the infrared exposure is given in Table VI. Oxygen enhances the Herschel effect on this emulsion at all relative humidities investigated.

As the data in Table III indicate, the infrared sensitivity of the pure bromide emulsion is more dependent upon relative humidity than is the white-light sensitivity. A more extensive investigation was made of the dependence of the infrared sensitivity on the relative humidity with both the pure bromide emulsion and the iodobromide emulsions. Both surface and internal image developments were employed. The infrared exposures were made in the same way as before, but exposures of several durations were used. The results obtained are given in Table VII. The densities obtained at 20% R.H. coincide, within the limits of experimental error, with those obtained at 52%. However, the infrared sensitivity of all three emulsions, both for surface and for internal latent-image formation, is considerably greater at 0% R.H. than at 20%.

Conclusions

The present work has produced a variety of results on the dependence of the Herschel effect upon humidity and oxygen. The general conclusions of each of the previous workers in the field are found to be valid for some particular emulsion and set of experimental conditions. The importance of humidity in determining the magnitude of the Herschel effect has been generally confirmed, and this factor must be accounted for in any general theoretical interpretation. The Herschel effect increases in going from 0 to 20% R.H. with all emulsions tested when the exposures are made in an atmosphere of nitrogen. The same statement holds when exposures are made in an atmosphere of oxygen for the emulsions which do not contain a desensitizing dye. This general trend is reversed, however, for the pure silver bromide emulsion containing pinakryptol yellow and bathed in 0.1 M potassium bromide.

The magnitude of the Herschel effect in the primitive emulsions shows little or no dependence upon oxygen. The same is true for the pure silver bromide emulsion. The magnitude of the effect in the commercial emulsion employed is larger in the presence of oxygen than in the presence of nitrogen. The Herschel effect in the pure silver bromide emulsion desensitized by pinakryptol yellow is greatly enhanced by the presence of oxygen for 0% R.H., whereas the Herschel effect is independent of oxygen for the same emulsion at 20% R.H. The situation evidently is complex.

Oxygen decreases the white-light speed of the primitive emulsions at low relative humidity, but has little or no influence at 52%. Oxygen has either no effect upon the speed of the chemically sensitized emulsions in the absence of desensitizer (e.g., the unbathed iodobromide emulsions) or it causes a small loss in sensitivity (e.g., the pure silver bromide and the iodobromide emul-

Table VI

Relative Humidity (%)	% Loss in Density	
	Nitrogen	Oxygen
0	3	14
20	8	40
52	11	33
79	10	42

Table VII

RED SENSITIVITY IN NITROGEN ATMOSPHERE

Relative Humidity (%)	Infrared Exposure (Min.)	Emulsions					
		C		F		H	
		0 M% AgI	1 M% AgI	0 M% AgI	1 M% AgI	3 M% AgI	0 M% AgI
		Surface	Internal	Surface	Internal	Surface	Internal
~ 0	0	0.07	0.07	0.15	0.07	0.13	0.05
	7.5	.19	.09	.37	.10	.32	.07
	15	.33	.10	.55	.14	.52	.08
	30	.51	.14	.75	.20	.74	.12
	60	.69	.18	.95	.27	.95	.16
	120	.87	.24	1.05	.37	1.10	.21
20	0	0.07	0.07	0.12	0.07	0.10	0.05
	7.5	.07	.07	.17	.07	.13	.05
	15	.09	.07	.25	.08	.21	.06
	30	.12	.08	.35	.10	.33	.06
	60	.15	.10	.46	.13	.45	.07
	120	.22	.12	.52	.16	.56	.09
52	0	0.06	0.07	0.12	0.06	0.10	0.05
	7.5	.07	.07	.17	.07	.14	.05
	15	.08	.07	.23	.07	.19	.05
	30	.11	.08	.33	.09	.29	.06
	60	.15	.09	.41	.12	.37	.07
	120	.19	.10	.50	.16	.45	.08

sions after bathing in 0.1 M potassium bromide). Both oxygen and humidity, however, have a marked effect upon the infrared speed. Whereas the density obtained by white-light exposure of the pure bromide emulsion decreases by only 17% on going from 0 to 20% R.H., the density obtained by infrared exposure at 20% R.H. is only about one-fourth that obtained at 0% R.H. Likewise, the density obtained by infrared exposure at 0% R.H. in oxygen is only about one-fourth that obtained in nitrogen, whereas the change in densities obtained by white-light exposure is less than 10%. Evidently both moisture and oxygen act to decrease greatly the infrared sensitivity of this particular emulsion. Both moisture and oxygen act to decrease the infrared sensitivity of the iodobromide emulsions, but the magnitude of the effect is smaller than with the pure silver bromide emulsion.

References

1. J. Narbutt, *Z. wiss. Phot.*, Vol. 28, p. 191 (1930).
2. M. Blau, *Phot. Kor.*, Vol. 71, p. 21 (1935).
3. A. S. Vnukova, *J. Phys. Chem. (USSR)*, Vol. 9, p. 598 (1937).
4. H. Bäckström, *Z. Naturforschung*, Vol. 6a, p. 377 (1951).
5. M. Thurston and J. M. Blair, *J. Opt. Soc. Am.*, Vol. 28, p. 348 (1938).
6. W. Vanselow, R. F. Quirk, and B. H. Carroll, *PSA Journal (Phot. Sci. and Technique)*, Vol. 18B, p. 11 (1952).
7. W. G. Lowe, J. E. Jones, and H. E. Roberts, "Fundamental Mechanisms of Photographic Sensitivity," Butterworths Scientific Publications, London, 1951, p. 112-125.

THE APPLICATION OF COLOR PHOTOGRAPHY TO A CLEFT LIP AND PALATE RESEARCH AND TRAINING PROGRAM

Frederick T. Sharp*

SEVERAL YEARS AGO, through a grant from the United States Children's Bureau, the University of Illinois set up a special program of education and training for persons whose professional activities relate them in any way to the treatment of cleft palate children. This activity is known as the Cleft Palate Center of the University of Illinois, Division of Services for Crippled Children.

The following quotation from a letter by Herbert Koepp Baker, Ph.D., Director of the Cleft Palate Center, describes the photographic need: "The problem of achieving an accurate photographic record of abnormal and normal conditions in the less accessible body spaces has been fraught with many technical and practical difficulties which have made the results of such photography clinically disappointing. In the research and diagnostic work related to deformities of the mouth and adjacent speech structures it has been our hope that chromatic rendition could be made accurate enough to make possible clinical judgments of the character of the tissue from the photographs themselves with some accuracy. Another essential detail of such photography is that the method and camera employed be sufficiently simple to operate so that an ordinary technical staff will be able to standardize procedures and produce consistently satisfactory results. Such photographs will be made of infants as well as adolescents and adults; equipment must be versatile enough to meet the unusual conditions characteristic of the clinic as well as the laboratory."

A consultation between all interested parties outlined the photographic aims of the clinic as follows:

1. The final form of the pictures would be determined by their use. There would be a need to: (a) Prepare prints suitable for case records. (b) Make enlargements for a broad teaching program and exhibits for professional meetings. (c) Produce both projection and display transparencies for teaching and exhibition.

2. Long life without deterioration of quality or color rendition is of paramount importance for: (a) Clinical records which may be needed in some cases for reference over as long a period as twenty years. (b) Filed master originals that may have to be reproduced for teaching or exhibit at any time in the future.

3. Certain physical characteristics would be required of the photographic equipment such as those offering: (a) Simplicity of operation so far as is compatible with the desired quality. (b) A mechanical means of positioning to repeat views of the facial structures so that they will closely match the x-rays taken at the clinic.

* University of Illinois Division of Services for Crippled Children, 1105 South Sixth Street, Springfield, Illinois. Presented at The PSA National Convention, New York, N. Y., 12 August 1952 as part of The Technical Division Symposium on Photography in Medicine and Biology. Received 10 October 1952.

(c) A perspective in intra-orals to match that of the normal view seen by the specialist in his clinical examination (d) A taking-speed high enough to stop motion even when the subject is a restless child.

4. Illumination should be: (a) Of a sufficient intensity for the use of a relatively high shutter speed at a small aperture for depth of field in the close-ups required. (b) Of consistent and reproducible color quality—regardless of voltage changes or other outside influence, and (c) Capable of being projected into the oral cavity in such a way that the size of the external opening will have a minimum effect on exposure.

5. The method of processing must have: (a) A high level of quality control. (b) A production speed sufficient to meet the needs of the clinical and teaching operations.

Many of the problems contained in the above outline are so interrelated that it is difficult to consider each by itself.

The Photographic System

Prints were chosen for clinical records, and there were many reasons for this. The long-term keeping properties of present color film have not been established, and the need for permanence was a high requirement. Again, the child is seen at many different places and by different people through the course of his examinations and treatments. Facilities for projecting and viewing transparencies are often unavailable at the time and place the child is being examined. Different sets of records



Fig. 1. Typical photograph at normal viewing perspective showing unilateral cleft lip (formerly called "hare lip") and palate. Illustration from the green record (magenta printer) of one-shot tri-color separation set.

will be used at different examining points. When projection facilities are at hand it has been observed that they are not used as often as might be desired. The exact opposite is true of prints inserted into a case record itself. An examiner will in almost all cases review the prints when he reads the written record. Also, the duplicating factor is simplified when prints are used, and in this work it is necessary to have several complete records for each individual. Only comparatively few of the pictures taken are enlarged or made into transparencies.

In choosing a printing process all those on the market today were thoroughly investigated. The dye transfer process best fitted the needs. It is capable of a satisfactory color rendition. The making of the necessary prints for multiple records, as well as reprints at later dates, is quick and simple. The production of enlargements by this process is no more difficult than the small record prints, and teaching slides are made by copying the prints on Ektachrome film. The use of dye transfer prints assures reasonable permanence since the separation negatives from which the matrix are made are on ordinary black-and-white film. These will keep indefinitely under any reasonable storage conditions.

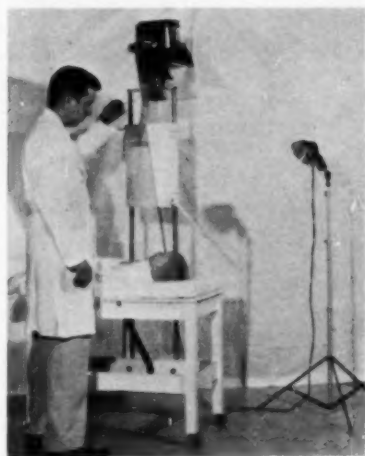


Fig. 2. Curtis 4 X 5 inch separation color camera mounted for taking profile and full face views of small children.

Separation negatives required for making the dye transfer prints can be produced in several ways. We chose the shortest and cheapest: This was the use of a "one-shot" or direct-separation camera. It was thereby possible to obtain excellent color prints with a minimum expenditure of time and material. On the other hand, the same result from a color transparency required the making of a time-consuming mask for the transparency before satisfactory separations could be made. The total cost in both time and material when working from a transparency is prohibitive and the results, are often less predictable. The separation camera also has a higher effective speed than color films. This analysis of cost would apply only where the volume of color printing is great enough to offset the original cost of the separation camera.

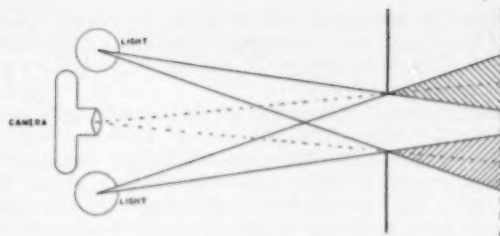


Fig. 3. Diagram of cross-lighting arrangement for cavity photography showing dependence of interior lighting on the size of the opening.

Our first separation cameras were equipped with standard Wratten, A, B, and C5 filters and occasionally required masking for critical work. A new set of filters recently developed by Curtis Laboratories has eliminated masking and somewhat improved the color rendition.

Most of the experimental work on the project was carried out prior to the release of the present Ektacolor process. This process in its present form is not capable of the degree of enlargement needed for our work, but it is capable of excellent color rendition. Where a large volume of work is contemplated, the present cost of Ektacolor also exceeds that which we are using.

When a child enters the clinic three or more pictures are usually taken. The minimum need would be met by a full face, a profile and an intra-oral exposure of each subject. If there is any significant difference between the left and right profiles, both must be taken. With some cases one intra-oral picture will suffice, but in many others it is necessary to take from two to five intra-oral views to completely demonstrate the whole interior of the mouth.

The pictures are taken from a normal viewing distance so the perspective is that customary on direct examination. See Figure 1. The views of the face are taken at approximately the same angles as the x-ray films produced by the custom-built infant cephalometer in use at the clinic. These photographs are made with a standard 4" X 5" Curtis One-Shot Color Camera, equipped with an 8 1/2" Commercial Ektar Lens and mounted on a bracket which centers it above an examining table. For this purpose the camera is used at a fixed distance, controlled by a vertical adjustment which moves the whole assembly. This adjustment brings a positioning pointer at the base of the camera support level with the nearest portion of the subject. The same camera is also used in the customary manner for most general color work required by the clinic. Figure 2 shows the camera in use.

Lighting for the facial photographs is simple, being standardized along the lines of the very familiar basic triangle system. Fixed lights are not used for these pictures since it is often necessary to modify the lighting to fit the individual situation.

Pictures within the mouth were not so simple to achieve. The procedural situation at the clinic makes it necessary to keep the process of taking the photograph as simple and rapid as possible. Exposures must be standardized, even though dealing with patients of all ages—from newborn infants to adults. To further com-

plicate the situation, surgery done on these children may have produced a tight upper lip which prevents the mouth from being opened as widely as would be possible for a normal child.

Many clinical photographic units have been built. None quite fitted our need. Many of these depend on two or more light sources placed near the camera lens. This arrangement will usually put the light where it is wanted. But because of the converging beams, the intensity of light reaching the posterior portion of the oral cavity is dependent upon the size of the opening. The light intensity is also conditioned by the size and shape of the cavity. Nevertheless, this system has some application.

Figure 3 is a simplified diagram of this type of lighting. The lights are projection lamps covered with a metal shield having a small aperture over the filament. The face of the subject is represented by the heavy vertical line and the required depth of field by the heavy vertical dotted line. The dotted lines from the lens into the opening represent the field being photographed. The central portion of this field receives the full illumination from both light sources and the shaded area is that receiving direct illumination from only one light. This procedure is capable of excellent results when the face and oral cavity are photographed together. It is less satisfactory in extreme examples as represented by a large child having a normal sized oral cavity with the extremely small opening produced by the tight lip.

Special Intra-oral Setup

With the arrangement described above acceptable results can be achieved but a constant variation of exposure is required to fit individual cases. Even after an operator becomes experienced, the results are not consistent enough for prints of good quality.

Experiments were made with a number of units including a camera placed in a large reflector with a single light source in the center of the reflector behind the camera. The results of this arrangement were somewhat similar

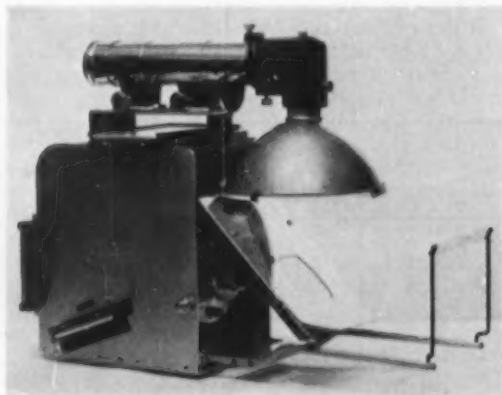


Fig. 4. Lighting arrangement of the separation camera used for intra-oral photography. A gray-scale mounted on the edge of the wire focus-finder is recorded along with the subject photographed. Objects lying within 4 inches of the scale are in focus.

to those achieved by two light sources placed near the camera lens. Several varieties of speed lights, including the ring light which fits around the lens, were tried. These were all eliminated since they could not consistently produce the required color quality, probably due to the discontinuous spectrum produced by lights of this type. When in the future a speed light is produced which overcomes this difficulty, it will be ideal because in our work children are a constant problem in subject motion.

A true axial lighting using a partial reflecting mirror would have been ideal, but the loss in effective illumination led to experiments with an opaque mirror set at 45° to the optic axis, directly in front of and facing away from the camera lens. A hole was cut in the mirror just wide enough to clear the viewing path of the lens, and a 750-watt spot light placed at 90° to the optical axis and trained on the mirror. This arrangement gives the effect of a camera looking down the center of a beam of light projected into the cavity being photographed. It was still necessary, however, to make exposure variations of one stop with extreme cases. The results were highly satisfactory.

Following the experiments with the rough assembly described, a unit was built which was carefully machined

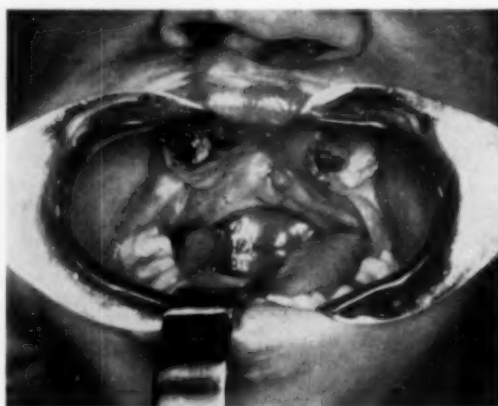


Fig. 5. Intra-oral photograph of 15 year old boy. Depth from lip to back of throat 9 centimeters. Black-and-white illustration from green record (magenta printer) negative of tri-color separation set.

to accurately locate all parts. This employed a 35mm (Leica) miniature camera with flash synchronization. The camera was mounted on a metal base to which was fitted a mirror as has been described together with a spot flash reflector for midjet bulbs. The choice of a reflector for a unit of this type is very important. Some tend to focus too large a portion of the light so that it is lost through the center hole of the mirror. The right one was sought by trial and error until one was found which gave an even illumination over the area to be photographed. At first an internally threaded tube placed through the hole in the mirror was used as a guard against flare. This was later discarded in favor of a little flat back paint applied to the edges of the hole.

Flash illumination was chosen to allow a high shutter speed at a small aperture. The necessary intensity in

Fig. 6. The intra-oral camera in use is almost always hand held to obtain the angle—different in each case—best adapted to show the subject.



tungsten light created too much heat for the comfort of the subject. The use of flash also eliminated the changes in color temperature caused by voltage changes in tungsten illumination. With this unit consistent results of very acceptable quality were achieved.

Prints as large as $16'' \times 20''$ were an occasional requirement. This made a film size of about $4'' \times 5''$ desirable. The eventual choice was a compromise to $2\frac{1}{2}'' \times 3\frac{1}{2}''$ using a 101mm Ektar lens, into which was

built a Waterhouse stop with an effective aperture of $f/90$. This represented the longest focal length of lens which would give the required depth of field at normal viewing distance.

The camera now used for intra-oral photography was specially built by Curtis Color Laboratories of Los Angeles, (see Figure 4). It is a direct separation $2\frac{1}{2}'' \times 3\frac{1}{2}''$ fixed focus unit with the flash and mirror mounted on the camera. It has a removable wire finder of the exact size of the area covered extending in front of the lens. This finder is located at the beginning of the area of acceptable focus so that anything from the wire frame to $4''$ beyond it will be in focus. A grey scale is built into the edge of the frame and hence appears in the picture. This provides a constant check in the development of separation negatives and acts as a standard for printing. The camera is usually hand held (Figure 6) since almost every picture is taken at a different angle to best show the condition being illustrated.

With this unit acceptable color prints as large as $14'' \times 17''$ from about 75% of the $2\frac{1}{2}'' \times 3\frac{1}{2}''$ film area are consistently produced. It has the great advantage of permitting photographically inexperienced personnel to expose excellent three-color separation negatives of difficult subjects. The technical photographic steps are then carried out by the experienced photographer in the photographic department.

This method of lighting and location of focus can readily be adapted to almost any camera which might be used for this type of work, and could be easily built in any good shop.

MORE PHOTOGRAPHY IN STEEL RESEARCH*

A modern blast furnace consists of a tall, rather conical tower constructed of brick and encased in steel. It is about 100 feet high and the internal diameter at the bottom may be as large as 30 feet. The brickwork at the base is about 3 feet thick. Such a tower is charged at the top with about 2,500 tons of iron ore, over 1,000 tons of coke, and 500 tons of limestone per day. At the base of the tower the charge is maintained at an incandescent temperature by a blast of air which is preheated to about 800C. Over 1,000 tons of liquid iron are tapped from the furnace every day. In view of the operating conditions of such a unit, it is not surprising that only little is known of what goes on inside.

Recently, on both sides of the Atlantic, the ciné camera has been used in an attempt to gain more information about the combustion zone. In the United States, Buchanan† has made a high-speed ciné study of the portion of the furnace visible through the "tuyeres," or nozzles, through which the hot-air blast is introduced.

On 15th January, Mr. C. Burns of the British Iron and Steel Research Association described to the Scientific and Technical Group of the Royal Photographic Society the preparation of a high-speed ciné-stereo record of the same zone.

The tuyeres are fitted with a heavy door in which a very small inspection window of blue glass is usually placed. For

this study, special doors with twin windows of fused quartz were used. Outside these windows a field-splitting unit of plane mirrors was placed, forming a stereoscopic pair of images on each frame of a Kodak high-speed ciné camera. The field of view was photographed in this way at up to 3,000 frames per second with an interocular distance of $5\frac{1}{2}$ inches. A beam-splitting unit was later developed which used the nature of the field of view to eliminate the vignetted zone between the right and left eye images which must normally be tolerated in this system of stereoscopic recording.

A new method of analysis was developed which operated on the image of a "still" from the film arrested in the projector. By this means interesting frames or particles for analysis could be chosen from the moving picture. The analyser produces by optical means a full scale 3-dimensional plot of the position of each particle examined. No intermediate numerical readings or calculations are required. It is claimed that an accuracy in the range of better than $\pm \frac{1}{3}$ inch is easily attainable, and the work of analysis is greatly expedited.

From this work, positive information was obtained on the existence and depth of the cavity opened by the air blast in the mass of particles of coke, ore and limestone in front of the tuyere. Particle tracks and velocities were charted and the circulatory nature of particle motion in the cavity also confirmed.

Mr. Burns' paper will appear in full in the May-June 1953 issue of the Journal of Photographic Science (R.P.S.).

* Communicated by G. I. P. Levenson for the Scientific and Technical Group of The Royal Photographic Society of Great Britain.

† R. A. Buchanan, Phot. Sci. and Tech., October 1952, page 66.

POLAROID INTEROCULAR CALCULATOR

Samuel Kitrosser*

THE INTEROCULAR CALCULATOR was designed to provide a simple tool for correlating some of the geometrical factors involved in stereoscopic photography. The Interocular Calculator has been used in the Polaroid laboratory for about seven years and several hundred are in the hands of professional stereo photographers. The following discussion shows how, with the help of the Interocular Calculator, stereograms can be produced having maximum tri-dimensional effect within the limits of comfortable viewing.

Preparation and Projection of a Stereo Slide

(a) *Photographic Exposure.* Figure 1 represents a stereo camera set up for making a pair of stereoscopic pictures. Points N and F represent the nearest and the farthest points of the subject from the camera. For the sake of simplicity, it is assumed that the far and near points are colinear with the point midway between the two lenses. This assumption simplifies the presentation of the geometrical situation and the derivation of the mathematical results. The final result, however, is in no way dependent upon this simplification, but holds for any relative position of the far and near points.

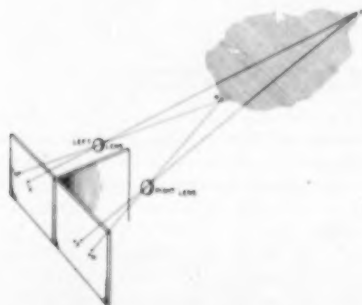


Fig. 1. Schematic arrangement of a conventional stereoscopic camera during exposure of the film. The nearest point N and the farthest point F of the object are recorded on photographic material as the homologous points N_L , N_R and F_L , F_R .

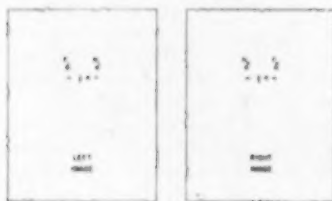


Fig. 2. The homologous points of N and F as they appear on the photographic record after the images have been inverted and transposed.

The left lens L and the right lens R will form respective images of points N and F at N_L and F_L and at N_R and F_R . These points are called the homologous points of N and F and the distance between them is $s/2$. Figure 2 shows the same points after the transparency has been inverted and the images transposed.

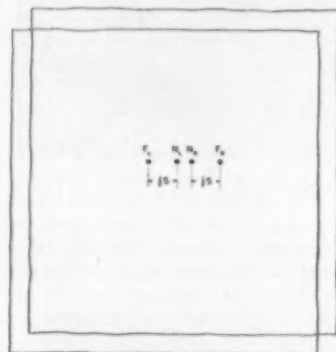


Fig. 3. The first step in registration of the images on the projection screen. If present, rotation and vertical shift of the images are eliminated.

(b) *Projection.* The pair of images is projected on a screen, superimposing the images as in Figure 3 so that there will be no rotation or vertical displacement of one image in respect to the other. At this point the images are aligned in a horizontal direction, superimposing the homologous near points and letting the homologous far points separate. The separation will be equal to S. Figure 4 shows this type of registration.

(c) *Viewing.* Figure 5 shows the viewing of the stereogram and the geometry of the reconstructed image. Viewing is done with the help of a system or a device which allows the right eye to see only the right image and the left eye to see only the left image. In this way the two planar images merge into one tri-dimensional image extending back of the surface of the projection screen. The nearest points will appear at the plane of the screen, but the depth of the image will depend on the separation S between the homologous far points.

The Relationship of the Maximum Separation to the Width of the Image

Let w be the width of the film image, and let W be the width of the projected image. Then

$$\frac{S}{s} = \frac{W}{w} \quad (1)$$

since both ratios represent magnification.

It has been found experimentally that, if the stereogram is to be viewed without visual discomfort, there is an upper limit to the horizontal displacement S for any given distance from the observer to the screen. Since this viewing distance normally is a function of the size of the stereogram, one can relate the value S to the width of the stereogram W. According to these experiments,

* Polaroid Corporation, Cambridge, Massachusetts. Presented at The PSA National Convention, New York, N. Y., 15 August 1952. Received 6 August 1952.

the maximum ratio of S to W consistent with comfort is approximately 1 to 24:

$$S \leq W/24$$

Since the separation S cannot exceed the average inter-pupilar distance of about 2.5 inches, one has

$$S = W/24, \text{ when } W < 60 \text{ inches} \quad (2)$$

and

$$S = 2.5 \text{ inches, when } W \geq 60 \text{ inches} \quad (3)$$

Then by combining the first three equations, one has

$$s = w/24 \quad W \text{ less than 60 inches} \quad (4)$$

$$s = (2.5 \text{ inches}) w/W \quad W \text{ greater than 60 inches} \quad (5)$$

Or, to use the convention that W is set equal to 60 inches in (5) whenever W is in fact less than 60 inches, then (5) holds for all values of W .

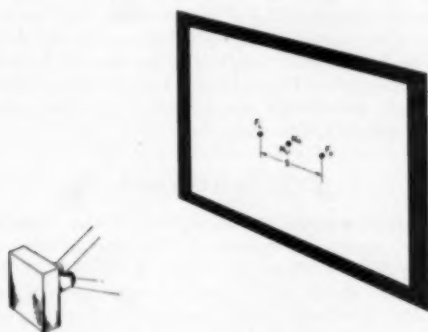


Fig. 4. Final adjustment of the images on the screen. Note that the homologous near points are superimposed and homologous far points are separated by distance S .

Table I

TYPICAL VALUES OF s AND S FOR DIFFERENT TYPES OF STEREOSCOPIC VIEWING CONDITIONS

Type of Viewing System or Device	Size of Image w	Ratio s/w	Value of s
6 by 13 cm. Stereoscope	60 mm.	$1/24$	2.5 mm.
Realist Type Stereoscope	24 mm.	$1/24$	1 mm.
	Size of Image W	Ratio S/W	Value of S
Vectograph	9 in.	$1/24$	$3/8$ in.
Projection, Image back of screen only	60 in.	$1/24$	$2\frac{1}{2}$ in.
Projection, Image forward of screen only	60 in.	$1/24$	$2\frac{1}{2}$ in.
Projection, Image forward and back of screen	60 in.	$1/12$	5 in.
Projection, Image back of screen only	15 ft.	$1/72$	$2\frac{1}{2}$ in.
Projection, Image back of screen only	30 ft.	$1/144$	$2\frac{1}{2}$ in.

In most cases, the images will be registered to appear beyond the surface of the screen. However, when the images are registered so that the stereoscopic image also extends forward from the surface of the screen, as illustrated in Figure 6 by the point VN , an additional amount of separation S can be allowed for the parts of the subject

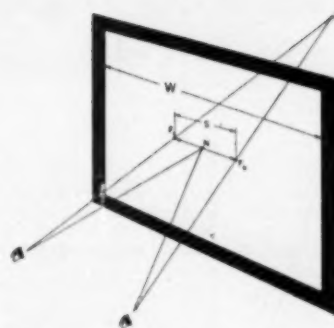


Fig. 5. Viewing of a projected stereoscopic picture. The point N will appear in the plane of the screen. The separation S of the far homologous points determined the distance at which the farthest point F will appear.

in front of the screen. For maximum stereoscopic effect for subjects extending on both sides of the screen, the preferred practice is to double S and to use equal amounts of horizontal displacement on either side of the superimposed homologous points.

The recommended values of maximum horizontal displacement will apply not only in the case of stereoscopic projection but also in almost all other types of stereoscopic viewing. Table I shows a few typical values for s and S for different types of stereoscopic viewing systems.

Table I indicates that the photographer should know something of the viewing system to be used before the negatives or transparencies are made in order to correlate the geometrical factors involved and to obtain a specific horizontal displacement. These necessary calculations are greatly simplified by the use of the Polaroid Interocular Calculator.

Polaroid Interocular Calculator

(a) *Geometrical Basis for the Calculator.* Figure 7 is a diagram on which the Calculator is based, where d = distance from lens to nearest point of subject

D = distance from lens to farthest point of subject

I = distance between taking lenses (interocular)

F = lens-to-film distance

From similar triangles we can write:

$$\frac{s}{2} = \frac{F}{d} \quad (6)$$

$$\frac{L}{D-d} = \frac{I}{D} \quad (7)$$

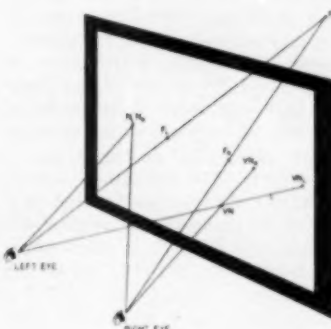


Fig. 6. Viewing of a projected stereoscopic picture when a part VN of the image appears between the observer and the screen. This requires that the right homologous point VNR be displaced to the left and the left homologous VNL point be displaced to the right so that the lines of sight cross in front of the screen.

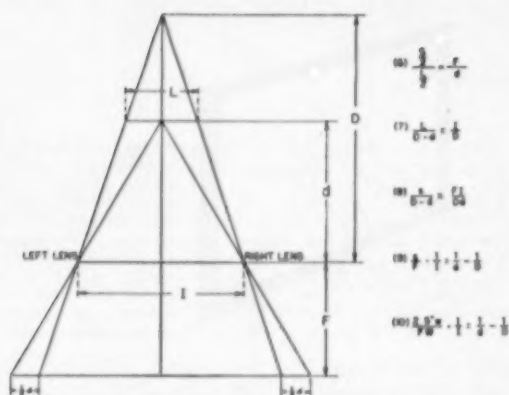


Fig. 7. Diagram of the stereoscopic arrangement illustrated in Figure 1. For the sake of simplicity of mathematical treatment, the far point, near point and the axis of the stereo camera are assumed colinear.

From (6) and (7) we get:

$$\frac{s}{D-d} = \frac{FI}{Dd} \quad (8)$$

or

$$\frac{s}{F} \cdot \frac{1}{I} = \frac{1}{d} - \frac{1}{D} \quad (9)$$

Substituting expression (5) for s , we obtain:

$$(2.5 \text{ inches}) \frac{W}{FW} \cdot \frac{1}{I} = \frac{1}{d} - \frac{1}{D} \quad (10)$$

In expression (10) we must continue to follow the convention that the symbol W is to be set equal to 60 inches whenever in fact W is less than 60 inches.

(b) *Construction of the Calculator.* This equation can be solved by a calculator consisting of a scale of reciprocals for obtaining the values of D , d , and I . The I scale is, in turn, connected with a system of logarithmic scales that serve to multiply

$\frac{1}{I}$ by the factor $\frac{2.5 W}{FW}$

In its finished form the Calculator is shown in Figure 8. The width of the projected image is indicated on Scale B. For images less than 5 feet in width or for images to be viewed on a stereoscope, the tab "A" is placed on the mark "5 feet or less." Scales C and D are determined by the characteristics of the photographic equipment; i.e., the film-to-lens distance and the width of the image in the camera. Scale G represents the values of the interocular distance and Scale E is used for both far and near distances from subject to lens. The suggested operating procedure is printed on the face of the Calculator.

(c) *The Use of the Calculator.* The Calculator can be used, not only for determining the interocular distance, but to determine any one of the distances involved if the others are known. This is very helpful in cases where the camera has a fixed interocular distance and non-

interchangeable lenses. The photographer can then simplify his work by establishing a set of distance limits for his subject material. Table 2 is an example of such a set of data, very similar to a depth of field table.

Table II

CAMERA 6 X 13 cm, 75 mm F. L., 65 mm I. O. Stereoscope Viewing		CAMERA 35 mm, 30 mm F. L., 75 mm I. O. Projection on 10" Screen	
Far Distance	Near Distance	Far Distance	Near Distance
∞	6' 6"	∞	13'
25'	5'	25'	9'
10'	4'	14'	7'
5' 9"	3'	8'	5'
2' 11"	2'	5' 9"	4'
		3' 10"	3'

The Polaroid Interocular Calculator is of greatest help to a photographer using a professional still or motion picture stereo camera with variable interocular distance. Having at his disposal a choice of lenses of different focal lengths to suit his artistic taste and the requirements of his subjects, he can use the Calculator to determine the correct interocular distance.

Acknowledgments

The writer wishes to thank all of the members of Polaroid Corporation who helped to prepare this paper, especially Mr. William H. Ryan, A.P.S.A., for his co-operation in developing the basic geometrical theory and to Dr. R. Clark Jones for his kind assistance and helpful suggestions.

References

- "Stereoscopic Photography" by Arthur W. Judge, Chapman & Hall Ltd., 1950 edition, pp. 417-455.
- "The Geometry of Stereoscopic Projection" by Professor John T. Rule, M.I.T., J. Opt. Soc., Vol. 31, No. 4, April, 1941, pp. 325-334.

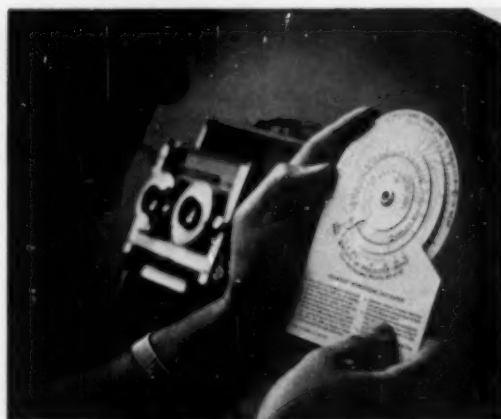


Fig. 8. Illustration by Roy Jacoby.

MODERN PHOTOMICROGRAPHY IN BRIEF REVIEW

Oscar W. Richards*

ABSTRACT

The nature of the specimen and the needs of the investigation determine the choice of the microscope. The camera adds a light-tight holder for the sensitive film and means for focusing. These may be simple or conveniently elaborate; of fixed or variable magnification. Assuming proper specimen preparation, illumination is fundamental to success. It is usually easier to use standard Köhler illumination than to approximate good lighting by trial and error. An ideal source should be uniform, of proper color temperature, readily magnifiable to fill the field and aperture of the microscope, and intense enough for short exposures. Use of zirconium and electronic flash sources and problems of color and of special microscopes (polarizing, fluorescence, ultraviolet, infrared, and phase) are discussed briefly.

TO SEE DETAIL TOO small for the unaided eye, one turns to the microscope. What is seen may be fugitive and require recording for future study, or records may be needed for filing, legal, publication, discussion, or teaching. For the first two and a half centuries of microscopy, these records were made by artists and, of necessity, included the artist's interpretation. Photographic recording is now the usual method for making such records. By proper choice of emulsions, the record may be made in color or black and white, and considerable control of detail is possible; for instance, red bacteria on a blue background may be photographed so the bacteria are either lighter or darker than the background. The photograph is only as valid as the integrity of the photographer.

Low magnification photographs are often made with a camera lens, or with an auxiliary magnifying glass. A long bellows is necessary. Microtessar, Microteleplats, and other special lenses have been made to give better images for this work. Considerable skill is required for proper lighting with photomicrographs, as magnifications up to about 20X (diameters) are called.

Greater magnifications are obtained with a compound microscope. Minimum equipment would be a spring back with focusing ground glass, film holder and a black cloth tube, or other means to keep nonimage-forming light from the plate or film. Some photomicrographic cameras are of fixed magnification; others have bellows and many adjustments which are of convenience for the user.

An ordinary camera may be used when the microscope is set at the proper tube length and is focused by a relaxed eye (or with an infinity telescope), and the camera lens is set for infinity. Small cameras may be balanced on the ocular of the microscope, but heavier cameras must be supported and protected from vibration. Since the camera lens is unnecessary, absorbs light, and may contribute aberrations, it is customary to use only the microscope lenses for photomicrography.

Specimens can rarely be examined efficiently without special preparation and competence with the microscope is of more importance than ability as a photographer. No unusual demands are made of photography by the properly adjusted microscope beyond ability to select,

expose, and process the photographic materials. Special photographic oculars have been designed to give a flat, distortion-free image. For pictures in natural color, apochromatic objectives and compensating eyepieces are preferable. The microscopist must be able to select the optics best adapted to the given problem. Far more care is necessary in aligning and lighting the microscope for photography than for vision, as a camera cannot compensate for glare, focus, etc., as the eye can do, or at least try to do, for us.

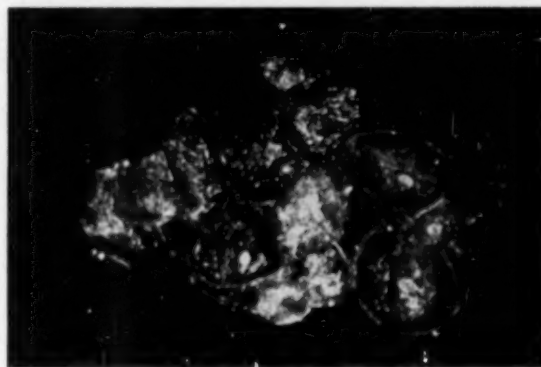


Fig. 1. Dark-field microscopy 450X of human squamous epithelial cells from the mouth.

The nature of the specimen determines the choice of the microscope and the illuminating system to be used, except the color temperature must be adjusted to the needs of the emulsion used in color photomicrographs.

An illuminator with a focusable lens system and an adjustable diaphragm (preferably iris) is desirable. Lamps may be of a coiled-coil or ribbon filament type providing that the system can fill the field of the lowest power and the aperture of the highest magnification objective to be used. Both field and aperture should be filled uniformly with light, but the Köhler method makes possible satisfactory photomicrographs with coiled filament lamps. The zirconium arc is a highly uniform source which has real promise for photomicrography. The optical and illuminating system must be accurately aligned for photomicrography, and it usually takes less time to do this correctly than to attempt compromise methods.

Colored specimens, or those with considerable optical path differences or absorption, may be seen with bright-

* American Optical Company Research Laboratory, Stamford, Conn., Presented at the PSA National Convention, New York, N. Y., 12 August 1952 as part of the Technical Division Symposium on Photography in Medicine and Biology. Received 24 October 1952.

Fig. 2. Fluorescence microscopy 750 \times of acid-fast material in lung from lipid pneumonia.



field microscopes; or the specimen may be stained so that it can be seen and photographed. The brightfield is often considered as the conventional light microscope, however, other kinds of light microscopes are equally important. The darkfield microscope is used, though photomicrographs are taken less often with it. See Figure 1.

The specimen may effect polarized light and appear in colors, or the specimen may be impregnated with a fluorescent chemical (Figure 2) and become selfluminous when it is irradiated with ultraviolet light. These polarizing and fluorescence microscopes are becoming increasingly useful. The fluorescent picture is useful as the eye is more sensitive to a small bright object against a dark background than the converse situation.

Transparent specimens may be revealed with the phase microscope (Figure 3), which has made possible the observation of unstained living organisms. However, sharp photographs require short exposures to stop normal swimming and Brownian motions. The electronic flash met this need; first with the FT-230, later with the FT-110 lamp. The photomicrographs obtained with the electronic flash are so sharp that it is now possible to measure accurately the size of living organisms and colloidal particles from such photographs.

Surfaces and, in some instances, internal detail can be studied by three-dimensional reconstruction of photographs made with the interference microscope. Other special microscopes utilize the higher resolution and chemical absorption specificity of ultraviolet, the penetration and structural chemical revelation of infrared, the x-ray beam, and, for very fine detail, the electron and proton microscopes. The wave lengths invisible to the eye require photomicrographs or other recording technics. Image converter tubes may be used to make the image visible and a television microscope is a reality. The conversion screens afford further control of contrast and may be photographed to provide photomicrographic records.

Stereoscopic pictures may be made with the monobjective microscope, either by tilting the specimen (low power), or using the half-aperture method (high magni-

fication). With the phase microscope stereoscopic pictures may even be made of living cells for study of how they are put together and to aid in the analysis of how they work. The bright and the B- contrasts have proven more satisfactory with the phase microscope for this application.

When the motion picture camera is used in place of the ordinary camera, one may make motion pictures through the microscope. The magnification of size is determined by the lens combination, but the speed at which the pictures are taken and later projected permit the microscopist to control time. This is very important, because, with living organisms, biological time may not be the same as our arbitrary clock time. By showing the pictures at a more rapid rate than they were taken, events that might take long periods of time may be reviewed in comparatively short sessions, or the reverse process slows down motions which are too rapid to be seen directly. The film gives a record which may be run time after time and different features of it watched until the observer has integrated the understanding of the whole process. The separate frames may be used for detail measurement, or for calculating rates. The film is of special use for analysis, for teaching and to show others what happened under the microscope.

Almost all kinds of emulsions are used in one or another kind of photomicrography. The slow- to medium-speed fine grain panchromatic films usually give the best results. The fastest films are used with electronic flash, light sources when necessary, and color films are needed when color is to be part of the record. For fluorescence photomicrographs, the daylight type of color film is preferable. Processing, in general, should give fine grain consistent with reasonable contrast. As with other kinds of photography, each specimen requires its own best treatment.

This is a brief sketch of some of the fundamental uses of photomicrographic records. Photomicrography is used in industry, as well as in biology and medicine; and it even has a role in art problems of picture evaluation. Much equipment has been designed for special work. Information may be found in the twenty volumes of the *Journal of the Biological Photographic Association*.

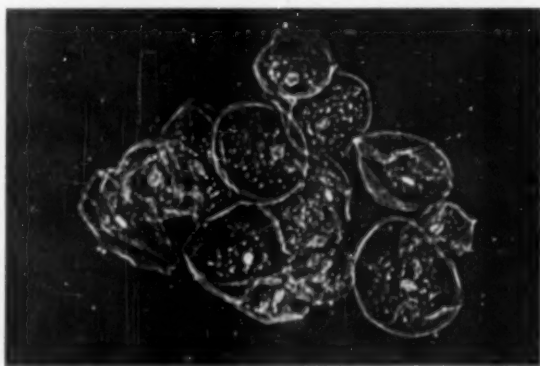


Fig. 3. Phase microscopy, bright contrast 450 \times of human squamous epithelial cells from the mouth. Compare with Figure 1.

MATERIALS OF CONSTRUCTION FOR PHOTOGRAPHIC PROCESSING EQUIPMENT*

L. E. Muehler and J. I. Crabtree, FPSA†

SUMMARY

General and selected sources are suggested for information on materials of construction, their properties, chemical resistivity, methods of testing, and fabrication. Factors in corrosion and types of corrosion in photographic processing are briefly considered. The detrimental effects of some metals and alloys on the processing solutions and processes are indicated. Outlines are given of qualitative corrosion and photographic tests of sample materials.

Metals and alloys as a class are generally superior physically for the construction of equipment but consideration of individual or single metals reveals that only a few varieties are suitable for processing and generally these are useful for only specific purposes. A classification of alloys into groups is made according to relative resistance to corrosion in the photographic field and general photographic utility. Selection among the "stainless" alloys is discussed in relation to the usual processing baths, and to some special processing solutions. Caution is urged in the use of clad metals while plated metals are generally contraindicated in favor of suitable homogeneous materials. Listings are given of metals and alloys generally unsuitable in developers, acid rinse baths and acid fixing baths, and bleach solutions containing ferricyanide and bichromate, respectively. Vitreous-coated metals chiefly in the form of fabricated vessels are briefly discussed.

S ELECTION OF A MATERIAL for the construction of any particular photographic processing apparatus or equipment, apart from its availability and cost, requires consideration of the following factors:

1. *The resistivity of the material to the most corrosive liquid which it will contact.* For example, although an ordinary 18-8 stainless-steel tank is quite satisfactory for containing developer, it will be rapidly corroded and pitted in certain areas when used with acid hardening, rapid fixing baths containing appreciable quantities of ammonium chloride.¹

2. *The effect of the material on the photographic properties of the solution.* For instance, a developer solution, when allowed to remain in a stainless corrosion-resistant metal tank soldered with ordinary tin-lead solder, may appear visibly unchanged; but when tested may fog an emulsion excessively, owing to the presence of tin salts dissolved from the solder.

3. *The conditions of time and temperature during which the solution is in contact with the material.* For example, bleaching and toning baths and solutions containing ferricyanides may contact stainless steel or Inconel alloy when used for short-duration or occasional service as with trays, troughs, reels, or small tanks, without ill effect, whereas rapid corrosion with resulting contamination of the solutions and perforation of the metal may occur in continuous service. For ultrarapid processing, temperatures up to 150 F may be employed in extreme cases.

4. *The adaptability of the material for construction purposes.* Glass, for example, when used alone and without special construction techniques, is unsuitable for large tanks because of its fragility and the difficulty of annealing it.

5. *The relation between choice of material and machine design.* The specific design of the processing machine or

other apparatus should accord with the type of material selected, otherwise expensive delays or handicaps in service may confront the user. An instance of this is in the design of a non-metal (plastic) bearing for service over a wide range of temperatures. Such a bearing should be placed on the outside of a frame of parallel supporting plates rather than on the inside, since the large coefficient of expansion of the material might cause it to bind or stall the mechanism when the temperature of the processing solution is raised.

Classification of Materials

Materials of construction for use in photographic processing and which are to be immersed in solutions, act as containers, or otherwise be exposed to the various processing baths or their vapors can be classified as metal materials, vitreous-coated metals, and non-metal materials. The latter may also include organic coatings and linings.

* Revised edition based upon an earlier version by J. I. Crabtree, H. A. Hartt, and G. E. Matthews (Amer. Phot. Vol. 18, p. 148, 1924) and subsequently revised (1943) as an insert for the Kodak Reference Handbook. The present revision includes information supplied by H. F. Betz, H. H. Brown, R. M. Corbin, C. E. Ives, H. B. Lea, J. C. Reddig, and R. S. Scott. The section "Notes on the Welding of Stainless-Steel Tanks" was revised by H. H. Brown, Metallurgical Laboratory, E. C. & M. Division, Eastman Kodak Co., Rochester 4, N. Y.

† Research Laboratories, Eastman Kodak Co., Rochester 4, N. Y. Presented at the PSA National Convention, New York, N. Y., 15 August 1952. Received 6 January 1953.

‡ For the purpose of this paper, stainless steel commonly known as "18-8" and sometimes called "ordinary stainless steel" consists essentially of a solid solution of metals in the form of an alloy of iron with chromium 18%, nickel 8%, and carbon approximately 0.1% or less.

§ Inconel alloy (The International Nickel Co., New York 5, N. Y.) nominally contains nickel 78.5%, chromium 14.0%, iron 6.5%, copper 0.2%, manganese 0.25%, silicon 0.25%, and carbon 0.08%.

Some References on Materials and Corrosion

In recent years, the number of new and improved varieties of metal and non-metal materials capable of resisting even quite corrosive chemical solutions has been greatly extended. Detailed information is available in many published papers and treatises. A useful reference on metals, alloys, and their structure and properties is the comprehensive Metals Handbook¹ which appears about every ten years. On the physical, chemical, and corrosion properties of metals, alloys, and non-metal materials, both in theory and in practice, may be cited the excellent Corrosion Handbook,² and also the Annual Chemical Engineering Construction Reviews of Industrial and Engineering Chemistry.³ Somewhat similar reviews may be found in Chemical Engineering.⁴ Excellent lists correlating trade names of materials with composition and manufacturer have appeared.^{5,6a} The magazine Corrosion, published monthly by the National Association of Corrosion Engineers, contains timely papers on various aspects of corrosion, testing, protective coatings and linings, and abstracts of the current literature on corrosion, attack, and protection of metal and non-metal materials.

Since many stainless alloys contain nickel, the publications of the International Nickel Company⁷ are useful for information on physical and corrosion properties of nickel and its alloys, including Monel alloy, Inconel alloy, and stainless steels. Pamphlets on corrosion testing methods, design of equipment, machining, and the fabrication of equipment are also available from this company.

Catalogs of construction materials and chemical process equipment, including tanks, piping, pumps, and other accessories, are given in the annual Chemical Engineering Catalogue.⁸ The Chemical Engineers' Handbook⁹ and other treatises^{10,11} present fundamental data, including information on chemical engineering equipment design, transportation of liquids and solids, process control, and materials of construction. For standard methods of analysis, testing, specifications of metals and non-metal materials, as well as reports of recent standardization committees, the Standards and Proceedings of the American Society for Testing Materials^{12,13} should be consulted. In the field of plastics, the annual Modern Plastics Encyclopedia¹⁴ is of value as well as The Corrosion Handbook,² Handbook of Plastics,¹⁵ and current texts on the variety of synthetic resins, plastics, and synthetic elastomers and their chemistry.¹⁶

An extensive volume on joining and fabricating metal equipment is the Welding Handbook.¹⁷ The leading steel manufacturers also supply excellent pamphlets on methods and techniques of welding stainless-steel alloys.

METAL MATERIALS

No common metal or alloy has yet been found which will resist corrosion completely in all photographic solutions; it is therefore necessary to restrict their use to specific purposes. Metal materials, however, possess desirable properties, such as ductility, non-fragility, strength, machinability, and ease of joining, which make them suitable to the fabrication and production of large-scale equipment, deep tanks, piping and process-

ing machines, as well as to the manufacture of small tanks, racks, film hangers, clips, reels, etc.

In selecting a material for equipment or tanks that will contact or contain photographic solutions, it is important, wherever possible, to choose a single alloy or metal rather than potentially dissimilar metals. This is good practice, since in the simplest case whenever two kinds of metal materials are used and they are electrically quite dissimilar in a given solution, potentials depending upon the nature of the solution will be set up between them (Table I).^{18,19} As a result, when the metals are in contact or are electrically connected, a current will flow and the corrosion propensity and rate of attack of one of them may be increased greatly, sometimes locally, and this fact must be taken into account when testing the chemical resistivity of the various metals or alloys.

The electrical-potential relation of the common metals and nickel and chromium alloys in solution has been given in a modified form of the so-called Electromotive or Galvanic Series (Table II).^{20,21} A method of decreasing electrolytic action between two different metals is to insulate them by interposing a non-conductor.

Factors Influencing Corrosion

The incidence and rate of corrosion depend upon many factors, such as the following:

- Nature and Condition of Material
 - Composition; surface finish; strains from bending, forming, or machining; welding or other joining; annealing or heat treatment; passivation-pickling treatment.
- Nature of Corroding Solution or Medium (Corrodent)
 - Ingredients; concentration; acidity or alkalinity (pH); oxidizing or reducing agents; liquid or vapor exposure.
- Temperature
- Time
- Agitation or Flow Velocity Effects
- Presence or Absence of Oxygen
- Electrolytic Couple
- Catalytic Metals or Ions
- Inhibitors
- Excessive Mechanical Stress

Types of Corrosion

Corrosion in connection with photographic solutions can be of several kinds: (1) *general*, in which the metal dissolves rather uniformly instead of locally; (2) *pitted*, a local form which may occur with eventual perforation of the material during contact with either solution or vapor over a sufficiently active solution; (3) *air-line*, attack at approximately the air-line of a solution in a partially filled container or conductor; (4) *vapor*, corrosion usually localized or pitted, for example, in the sulfur dioxide-containing aqueous condensate over an acid fixing bath in a more or less confined, partially filled vessel or pipeline; (5) *intergranular*, corrosion occurring in solution or vapor, frequently with improperly annealed or unstabilized stainless steels and usually to a greater degree with such alloys having carbon content greater than 0.03%, corrosion arising from attack in or near the carbide-rich areas at the microscopic grain boundaries of the metal structure; (6) *electrolytic*, due to metallic coupling with another metal that is considerably removed in potential from itself, for example, one rather far removed in relative position in the electromotive force (emf) series of metals or the galvanic series of

Table I

ELECTROMOTIVE SERIES

Metal	Molal Electrode Potential in Acid Solution at 77 F (25 C)	
	Ion	Volt
Magnesium	Mg ⁺⁺	-2.37
Aluminum	Al ⁺⁺⁺	-1.66
Zinc	Zn ⁺⁺	-0.76
Chromium	Cr ⁺⁺⁺	-0.74
Iron	Fe ⁺⁺	-0.44
Cadmium	Cd ⁺⁺	-0.40
Nickel	Ni ⁺⁺	-0.25
Tin	Sn ⁺⁺	-0.14
Lead	Pb ⁺⁺	-0.13
Hydrogen	H ⁺	Arbitrary zero point
Copper	Cu ⁺⁺	+0.34
Silver	Ag ⁺	+0.80
Mercury	Hg ⁺⁺	+0.85
Palladium	Pd ⁺⁺	+0.99
Platinum	Pt ⁺⁺	+1.2
Gold	Au ⁺⁺⁺	+1.50

metals and alloys (see Tables I and II); (7) *contact or crevice*, localized corrosion, usually of the pitted variety, common with ordinary stainless steels and promoted by close contact with some non-metal material or in crevices where the solution has no extensive motion relative to the metal; (8) *friction and cavitation*, corrosion effects occurring in bearings, pumps, and devices with relatively high solution velocities or impingement; (9) *strain*, attack resulting from sharp bending, forming, or machining without proper subsequent heat treatment;* and (10) *stress*, chemical attack due to continued excessive mechanical stress.

Detrimental Photographic Action of Certain Metals and Alloys

The possibility of chemical fogging or of an undesirable photographic action of certain metals and their alloys should be clearly kept in mind when approaching the selection of constructional material which will contact even the usual processing solutions. The chemical-reducing power of aluminum and aluminum alloys in alkaline developers is sufficient to generate sulfide in small amounts capable of promoting the development of objectionable stain and fog in fresh and used developers of sodium carbonate alkalinity. Copper, and alloys of it such as brass and bronze dissolve in developers to give traces of copper. In concentrations even lower than 1 in 1,000,000 parts of developer,† copper (1) promotes more rapid aerial oxidation of the solution than is shown in its absence, and (2) causes aerial fog in unexposed areas when films are alternately immersed and exposed to the air several times during development.

Metals notable in producing chemical fog are tin and its alloys, including ordinary solders. These need only be present in a given developer from a few hours to a day or more at ordinary room temperature to give percep-

* High-temperature annealing (approximately 1800-2000 F), followed by rapid quenching, in the case of stainless steels.

† In certain developers low in sulfite the effects of copper can be shown at a concentration of 1 part of copper in 4,000,000 parts of developer.

Table II

GALVANIC SERIES OF METALS AND ALLOYS

CORRODED END (Anodic, or least noble)

Magnesium
Magnesium alloys
Zinc
Aluminum 2S
Cadmium
Aluminum 17ST
Steel or Iron
Cast Iron
Chromium-iron (active)
Ni-Resist alloy
18-8 Chromium-nickel-iron (active)
18-8-3 Chromium-nickel-molybdenum-iron (active)
Lead-tin solders
Lead
Tin
Nickel (active)
Inconel alloy (active)
Hastelloy C alloy (active)
Brasses
Copper
Bronzes
Copper-nickel alloys
Monel alloy
Silver solder
Nickel (passive)
Inconel alloy (passive)
Chromium-iron (passive)
18-8 Chromium-nickel-iron (passive)
18-8-3 Chromium-nickel-molybdenum-iron (passive)
Hastelloy C alloy (passive)
Silver
Graphite
Gold
Platinum

PROTECTED END (cathodic, or most noble)

tible or intense fog, depending upon the proportion of tin in the material and the duration of contact.

Zinc, as in galvanized ware coatings, can impart intense chemical fogging power to a developer but only when the metal has been in contact with an acid sulfite-containing solution, such as sodium bisulfite or formaldehyde bisulfite which is sometimes a component of a stock solution for preparing a developer. Here, the zinc produces sodium hydrosulfite, a trace of which produces a high degree of fog in the usual developer.

Metals and alloys that readily and undesirably plate out silver from used fixing baths include copper, brass, bronze, ordinary iron or steel, lead, Monel alloy, nickel, and zinc. These metals are therefore unsatisfactory for film clips or hangers, or chains for transporting paper or other materials through the baths in continuous processing machines. Even when these metals are washed after being in the fixing bath, the accumulated silver coating retains or occludes enough silver thiosulfate complex compounds to decompose or be removed in the alkaline solution and thus contribute traces of sulfides and thiosulfates in used developers sufficient to promote the development of yellow stain or fog in film or fog on papers.

Corrosion and Photographic Tests of Sample Materials

Easily conducted accelerated tests of metal and non-metal materials such as those described below are qualitatively valuable in selecting materials for a given type of photographic service.²³ Such a qualitative test of a particular sample will usually give information regarding (a) relative corrosion or resistivity of the material, and (b) its possible detrimental action on the photographic solution.

Further data can be obtained by practical trials or by testing multiple samples in special holders under practical conditions.^{23,24} However, over a long period of experience, the results of accelerated tests of the type described have been confirmed in practical use. Comprehensive quantitative methods for laboratory testing of metals and non-metals are described in the Corrosion Handbook.³ For total immersion tests of stainless steels with quantitative measurement of weight changes, an A.S.T.M. Tentative Method has appeared.²⁵ A recent text also presents the subject of corrosion-testing procedures.²⁶

(a) *Preparation of the Sample.* To make a qualitative accelerated test, a representative piece of metal or alloy,* for example, a sheet 1 inch wide by 3 to 5 inches long, preferably cut by shearing, should be cleaned free from oil or grease by immersion in benzene (benzol) for about 1 minute, and dried with a clean cloth. The specimen strip is then half immersed in a definite volume of the particular photographic solution to be tested, contained in a clear wide-mouthed bottle (4 to 16 ounces, depending upon the sample length), so that each square inch of total area of the material will have approximately 1 to 3 ounces of solution for contact. Only one sample should be placed in this solution. The bottle may be (a) tightly stoppered, (b) loosely stoppered, or (c) left open, depending on the information desired. When the bottle is closed, the severity of the test is increased because of the more concentrated vapor phase, and such a test has proved valuable in studying the action of acid fixing baths on various stainless steels and similar materials. However, in studies of the fogging properties of metals and alloys on developers, it was found desirable that the bottles at room temperature be open to access of air, to secure the maximum effect with some materials.

(b) *Comparison Alloys for Test.* In testing metals and alloys, it is desirable to include for reference samples of alloys, such as Type 304† and Type 316 stainless steels with 2B or No. 4 finish, prepared as just described, immersed in duplicate samples of the particular solution, and kept under the same conditions for observation.

* Free from impurities, such as ordinary iron, copper, etc. For passivation treatment of stainless alloys, see manufacturers' instructions or the Corrosion Handbook, H. H. Uhlig, editor, John Wiley & Sons, Inc., New York, 1948, p. 158; also a subsequent section of this paper.

† Wrought stainless steels are usually referred to by a "type" number as given by the American Iron & Steel Institute (AISI) which identifies the material in a given analysis range. Stainless-steel cast alloys have separate identifying "designations" as given by the Alloy Casting Institute. For correlation of AISI types and ACI designations with analyses, see The Corrosion Handbook, H. H. Uhlig, editor, pp. 1150-1151 (1948), John Wiley & Sons, Inc., New York, N. Y., or Ind. Eng. Chem., Vol. 40, pp. 1903-1913 (1948). For a revision of the composition of AISI Type 316 as of April 16, 1947, see Materials and Methods, Vol. 25, p. 125 (1947).

(c) *Storage and Testing.* Duplicate tests should be made at ordinary room temperature, for example, 70 F (21 C) and at 110 F (43 C) and should be continued with observations after 18 to 24 hours, 2 days, 4 days, 1 week, 2 weeks, and 1 month or longer. The results at high temperature should not be regarded as quantitatively conclusive but rather as indicative. Materials intended for ultrarapid processing service may require testing at temperatures as high as 130 to 150 F (55 to 65 C). In any case, the photographic properties of a given solution should be compared with those of an equal volume of the solution stored in a container of duplicate dimensions under the same conditions but without the material under test. In the case of a developer, this can be done by developing two pieces of identically exposed film‡ for the recommended time, one in the test solution, the other in the control solution. The negatives can then be compared for fog, contrast, speed loss, etc. Details of tests of a series of metals and alloys for their fogging action on several developers have been published.²⁷

Observations should be made regularly as indicated during the progress of the test, the appearance of the samples should be noted, and if a developer is being tested, its fogging tendency should be determined at 68 F (20 C) by developing in it a film with a representative unexposed area for the usual recommended time. If necessary, water should be added and mixed with the solution at frequent intervals to replace that lost by evaporation. Care should be taken to remove the test material when adding water or removing the solution for tests or replacing it. When only resistivity is being studied, a fresh lot of the solution being used may periodically replace the original volume. The condition of the metal should be noted in the portion exposed to the vapor as well as that immersed in the solution. Also, the area in the vicinity of the air-line of the solution should be noted for any corrosive effect.

(d) *Effect of Nature of Solution on Corrosion.* Important factors with developers are the alkalinity (pH) of the solution and the concentration of sulfite. Representative developers with increasing alkalinity and covering the general range of proprietary preparations are Kodak Developers D-76, DK-60a, D-72 (various dilutions), D-19, and D-8. The developers of intermediate alkalinity (DK-60a and D-72) are well suited to a study of the effect of copper and other metals in giving rise to aerial fog and inducing aerial oxidation of the solutions.

For testing the action of fixing solutions, it is desirable to employ both fresh and partially exhausted samples of the particular type of solution. Representative types are the widely used Kodak Acid Hardening Fixing Bath F-5 and the Kodak Chrome Alum Fixing Bath F-23. Rapid fixing solutions may be represented by Kodak Rapid Fixing Bath F-7 which contains ammonium chloride,¹ and Kodak Rapid Liquid Fixer and Hardener which contains ammonium thiosulfate.

Other solutions, such as bleach baths and toners, can be tested for action on metals as outlined, with additional tests to simulate practice. In any case, the photographic properties of the solutions should be determined by processing similar pictures or film strips both in the solution in question and in a control lot subjected to the same conditions but without the metal.

‡ Each film should have a series of graded exposures and an unexposed area.

(c) *Tests with Lacquers and Plastics.* Tests similar to those described can be used to test protective lacquer or paint coatings on metal and non-metal materials. The use of closed containers at 110 F (43 C) may be necessary, as for example, to show the effect of highly alkaline developers on certain plastics or, in the case of ordinary developers, to leach fogging or density-depressing compounds from rubber and similar products.

In addition to determination of the resistivity of the material and its effect on the photographic solution, observations should also be made of any tendency to chip away or distort with increased temperature.

In the case of non-metal materials, any tendency to soften or swell should be noted. This is particularly important for materials to be used in the ultrarapid processing service, in which case the testing should simulate conditions under which the temperature may reach 150 F (65 C).

A method of testing plastics for resistance to a number of chemical reagent solutions has been recommended by the American Society for Testing Materials.²⁸ This testing body has also published specifications for and methods (principally physical) of testing plastics, together with nomenclature and definitions.²⁹

Metals and Alloys

The early work in these Laboratories by Crabtree and Matthews³⁰ on the corrosion and photographic action of a variety of single metals and some alloys on solutions such as developers and acid fixing baths, served to indicate offending metals to be avoided either as single metals or as predominant constituents of alloys, and to indicate several useful metals and alloys. The results of further investigation with Hartt^{31,32} also emphasized the importance of avoiding electrical couples of dissimilar metals or alloys. Furthermore, plated metals were found unsuitable for general use.

It is not feasible in this treatise to catalog all of the various kinds and types of metals and alloys which have been considered and tested in photographic solutions. However, many individual metals and representative types of alloys will be given. Single metals are considered first, although their utility is usually confined to rather restricted purposes. In general, for maximum resistance to corrosion and wider application, the number and variety of stainless alloys useful for corrosion-resistant equipment is so impressive in recent years as to make this class of metallic materials of prime importance for consideration in constructing processing apparatus.

Most of the materials in the various listings have been tested in the laboratory for corrosion and deleterious action in photographic solutions and many of the more promising ones have been tried or observed in practical use. A few materials are also included which show promise in resisting certain chemical solutions.

Value of Various Metal Materials

The practical applications of the results of testing various single metals, alloys, clad, and plated metal materials will now be considered.

(1) *Single Metals.* In the earlier work cited,^{30,31,32} lead and nickel were the only single metals which appeared to be of any special importance for use with photo-

graphic solutions, although iron was found of some value with developers.

Lead and nickel tanks or linings and lead, nickel, and wrought-iron piping can be used satisfactorily for most developing solutions, although lead is attacked by strongly alkaline developers. Iron is attacked more or less by most developers in the presence of air and tends to form oxides and hydroxides in the solution so that it is important to filter out such particles before use and to keep pipes filled with developer. Lead may be used for lining storage or solution-replenishing vessels for fresh unacidified sodium thiosulfate or acid fixing solutions which do not contain silver. Neither lead nor nickel should be employed for acid fixing solutions in use, since the metals are slowly attacked, become coated with silver, and must eventually be replaced. Sheet lead is sometimes used for lining temperature-controlling vessels used in x-ray work where tanks of stainless steel are in direct contact with the lead. Sheet lead for lining small tanks may be used for ferricyanide-bromide bleaching solutions and likewise the proprietary bleaches employed in the processing of Kodak Ektachrome and Kodak Ektacolor film.

In view of recent practical observations on the resistance of copper to ferricyanide-containing bleaching solutions used in color processing, it is evident that this metal can be used for tank linings for such solutions and, in addition, for tanks and piping for such solutions within the limitations of the softness of the material (see also red brass in section on alloys).

From recent work, other single metals appear to be promising. Silver, although itself too soft for structural use, withstands continuous contact with developers and has been used as a clad material on steel.^{34,35} Tantalum has been commercially produced for some time and is gaining in use in the chemical industry³⁶ for linings, pipe coils, and immersion heaters, pump parts, thermocouple walls, etc., to withstand the action of strong acid reagents such as hydrochloric acid. It is still rather costly but is available in various forms, including thin sheets, rod, and seamless tubing.* Tantalum is rather unique in that in tests it did not exhibit any signs of attack with mildly alkaline developers and a large variety of acid photographic solutions, including corrosive oxidizing and acid bleaching solutions. It is, however, attacked readily by strongly alkaline solutions.

Titanium is another promising metal for general corrosion service and may find photographic application. The estimated price of the commercially pure metal formerly produced experimentally at \$15 to \$30 per pound in primary fabricated rod and sheet form was conditioned by methods of limited production and manufacture.³⁷ However, research, development, and promotion by the United States Bureau of Mines and by several private agencies toward improved large-scale commercial manufacture of the metal may eventually serve to lower the price significantly, to possibly one-tenth of this value. The metal is strong and light. In its ductile form it is about 1.7 times as heavy as aluminum and only about 0.6 times as heavy as stainless steel. It appears to lie between Monel alloy and Inconel alloy (passive form) in the Electromotive or Galvanic Series of metals and alloys.

Titanium shows corrosion resistance^{38,39} suggestive of the behavior of ordinary stainless steel, frequently with

* By Fansteel Metallurgical Corp., North Chicago, Ill.

Table III

SUITABILITY OF SINGLE METALS IN PHOTOGRAPHIC PROCESSING SOLUTIONS (CONTINUOUS SERVICE)

Metal	1D	2D	AR	ACr	1F	2F	3F	W	Special
Aluminum	N	N	N	N	N	N	N	N	Distilled water
Copper	N	N	N	N	N	N	N	N	Ferricyanide bleach
Iron	r	r	N	N	N	N	N	N	Use only with closed, filled piping for developers
Lead	R	N	N	N	N	N	N	N	Ferricyanide bleach
Nickel	R	R	N	N	N	N	N	r	Distilled water
Silver	R	R	R	R	N	N	N	R	
Tantalum	R	N	R	R	R	R	R	R	Acid-oxidizing bleach
Titanium (tentative)	R	R	r		r	r		R	Acid-oxidizing bleach Ferricyanide bleach
Tin	N	N	N	N	N	N	N	N	Distilled water
Zinc	N	N	N	N	N	N	N	N	Galvanized tap-water piping

KEY TO ABBREVIATIONS

Abbreviation	Recommended or Type of Solution	For example Kodak Formula
R	Recommended	
r	May be used with reservations or in the case of certain stainless alloys not suitable in locations such as closed or covered tanks or systems where moist sulfur dioxide vapor is present over solutions	
N	Not recommended	
1D	Carbonate-containing or similar moderate-alkalinity developer	D-19; D-72 (1:1)
2D	Caustic developer	D-8
AR	Plain acetic acid rinse or stop bath	SB-1a
ACr	Acid chrome hardening rinse or stop bath	SB-3
1F	Acid aluminum hardening fixing bath	F-5
2F	Acid aluminum hardening rapid fixing bath (containing ammonium chloride)	F-7
3F	Acid chromium hardening fixing bath	F-23
W	Washing	

The recommendations are made with the assumption that continuous service or an unlimited time of contact of the material with the solution is expected. Other service may be regarded as either intermittent or occasional.

general rather than pitted corrosion and other notable exceptions. Significant performance is represented in its resistance to solutions containing active chlorine and hypochlorites, highly oxidizing reagents, chloride salts, cupric chloride, ferric chloride, sulfur dioxide, and sodium sulfide. A very low rate of attack has been shown in 5 per cent solution of hydrochloric acid, acetic acid, ammonium hydroxide, and sodium hydroxide. Titanium metal is unfortunately readily attacked by sulfuric acid, the rate increasing with concentration.³¹ On the basis of the chemical evidence, the photographic value of this metal would appear to be near that of Type 316 stainless steel and even superior to this alloy in certain instances;³² for example, in its resistance to attack by ferricyanide bleaching solutions such as are used in color processing and toning. Meanwhile, the practical use of titanium as well as its utility with special solutions, including those containing sulfuric acid, will require further investigation. Fabrication techniques for titanium are not yet well established.

Table III summarizes present recommendations on the photographic uses of single metals in various processing solutions.

(2) *Alloys.* The detrimental photographic action on developers of certain alloys, Duralumin and other aluminum alloys, brass and bronze, and tin-lead solders has been treated in a previous section.

On the basis of tests and practical experience, the various alloys can be classified generally into groups, as follows, according to their photographic corrosion-resistance and versatility and also to some extent with reference to their principal metallic constituents.

Classification of Alloys.

Group N—Not generally resistant or acceptable, but some varieties may be used for restricted purposes.

Brass, yellow and red (copper-zinc)
Duralumin alloy (aluminum-magnesium-copper)
Nichrome alloy (various nickel-chromium-iron)
Nickel Silver, previously called German Silver (nickel-copper-zinc)
Phosphor Bronze (copper-tin-phosphorus)
Silicon Bronze (copper-silicon)
Soft Solders (various tin-lead)
Brazing, Silver Solders (silver-copper-zinc with or without cadmium)
Type Metal (lead-tin-antimony)

Group LR—Limited resistance except for particular service.

Duriron alloy (iron-silicon in cast form only)
Durichlor alloy (iron-silicon-molybdenum in cast form only)
Monel alloys (various types nickel-copper with small amounts of iron, manganese, silicon, and sulfur or aluminum and titanium)
Ni-Resist alloys (various types, e.g., nickel 15.5-copper 6.5-carbon 2.8-chromium 2.5-silicon 1.8-manganese 1.3-iron, balance)

Group MR—Moderately resistant but undesirable in certain applications.

Inconel alloy (nickel 79.5-chromium 14.0-iron 6.5)
Incoloy alloy (nickel 34-chromium 21-iron, balance)
Stainless Steel Types 302, 303, 304, 308, 309, 310, 321, 347 (various alloys from approximately chromium 18-nickel 8-iron to approximately chromium 25-nickel 20-iron)

Group HR—Highly resistant.

Stainless Steel Type 316 (chromium 18-nickel 10-molybdenum 2.0 to 3.0-iron)
Stainless Steel Type 317 (approx. chromium 20-nickel 14-molybdenum 3 to 4-iron)

Group XHR—Extra highly resistant.

High chromium-nickel-molybdenum complex alloys represented by Carpenter 20, Chlorimet 2, Chlorimet 3, Durco D-10, Durimet-20, Hastelloy C, Hastelloy D (in cast pipe and fittings only), Illium G (cast form only), and Worthite alloys
Extremely hard cast cobalt-base alloys containing chromium and either tungsten or molybdenum represented by various varieties of Haynes-Stellite alloys

Of the numerous known alloys, Inconel alloy³³ and the austenitic stainless steels,⁴⁰ such as 18-8 (Type 304) and a member of the relatively non-pitting variety containing molybdenum (Type 316), are the principal alloys which have been adopted for photographic use.

A new and specialized use of red brass (copper 85% or more) and the silicon bronzes† in resisting the action of ferricyanide-containing bleach solutions has been demonstrated in practical large-scale processing, principally for piping and valves, but also for tanks and tank linings. Small tanks have been fabricated by soldering, while large tanks have been welded, using high copper-

* By The International Nickel Co., Inc., 67 Wall St., New York 5, N. Y.

† Such as Everdur bronze and other silicon bronzes.

brass welding rod. It should be noted that yellow brass fails in ferricyanide bleach service, so ordinary valves which employ yellow-brass valve stems are not suitable. For such solutions, the Saunders Patent Valves* with Everdur bronze body and Neoprene elastomer diaphragm are very satisfactory. A disadvantage in the use of red brass, silicon bronze, or copper for ferricyanide service is the formation on the metal of the semi-adhering but somewhat protective precipitate of red, insoluble copper ferrocyanide. Since most of this material is easily rubbed off or dislodged, filtering is often required, particularly in large systems. High flow velocities or the presence of undissolved solids can cause excessive rate of corrosion by removing the copper ferrocyanide from the metal surface.

The alloys herein classified as exhibiting limited resistance (Group LR) include Duriron,† Durichlor,‡ Ni-Resist,§ and Monel alloys.† Duriron and Durichlor alloys are extremely hard and brittle high silicon-iron alloys, the latter containing about 3% molybdenum, which confers increased resistance to hydrochloric and other strong acids. These alloys, available only in cast form, are useful for drain pipes and sewers where resistance to chemical agents is required. Ni-Resist alloy, a cast alloy of iron with one variety containing approximately 15% nickel, 6% copper, and 2% chromium, has been used to some extent by the motion-picture processing industry for pumps, valves, and drain pipes.⁴¹ It has the advantage of being somewhat softer and more readily machinable than the high silicon-iron alloys, such as Duriron alloy, but is less resistant than these to the attack of strong acids.

In the United States, Monel alloy is less generally used in photographic apparatus than previously but may be employed for certain solutions and operations: developers, acetic acid stop baths, and for washing vessels and tanks. The alloy is easily machined and for shafts, bearings, or sliding contact service does not seize or gall like the stainless steels. Even rolled Monel alloy will seize under certain conditions in contact with itself and with certain other metals.⁴² Monel alloy, however, should not be used for certain alternately immersed clips, hangers, chains, or paper-transporting pin-bars, etc.; silver becomes plated out on the alloy and thiosulfates are adsorbed and later released in developers to produce stain or fog as described above. Monel alloy also corrodes rapidly in ferricyanide-bromide and acid bichromate bleach solutions.

Inconel alloy and the stainless steels Types 302, 303, 304, 308, 309, 310, 321, and 347 are alloys which may be classified together as moderately resistant (Group MR). These passive and continuously bright alloys are resistant to developers and are superior to Monel alloy for use with acid fixing baths in open vessels, either fresh or with the acidity maintained during use; they are not so susceptible to general or air-line corrosion and do not plate out silver with exhausted fixing baths and become attacked as does Monel alloy. An exception in the case of selenium-containing Type 303 may be noted since corrosion in acid stop baths and acid fixing baths has been reported with this alloy.

* Available from the following firms: Grinnell Co., Inc., Providence, R. I.; Hills-McCanna Co., 2345 W. Nelson St., Chicago 18, Ill.

† By The Duriron Company, Inc., Dayton 1, Ohio.

‡ By The International Nickel Co., Inc., New York 5, N. Y.

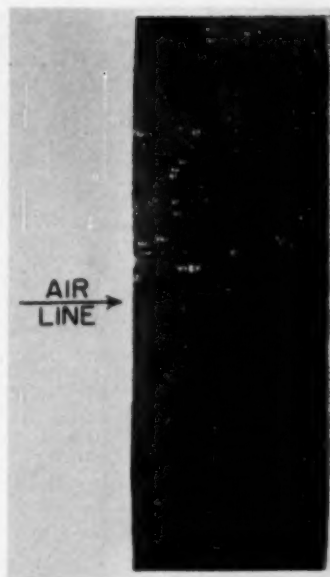


Fig. 1. Pitted Corrosion of 18-8 Stainless Steel, Type 304, from Action of Confined Vapor over Acid Fixing Bath.

With acid fixing baths, all of the alloys of Group MR are attacked and pitted in the vapor over the solution, as indicated in Figure 1, particularly when the vessels have been closed for sufficient time. This action increases either with acidity or the presence of chloride ion together with ammonium salts (ammonium chloride or ammonium thiosulfate) so that this group of alloys should not be used for chrome alum fixing baths or rapid fixing baths which contain ammonium and chloride ions. Variations in room and solution temperatures increase the tendency for this corrosion probably because of the action of water vapor containing sulfur dioxide condensed on the surface of the metal.

To be used successfully as containers for the ordinary acid fixing baths with Inconel alloy and the non-molybdenum austenitic stainless steels represented by the 18-8 variety (Type 304) with low carbon content (0.08% max) the vessel must be either (1) entirely filled with solution, (2) essentially filled with solution and without a cover at all times so as to be open to the free movement of air, or (3) used intermittently and thoroughly washed and cleaned regularly.

Marked improvement toward indefinitely resisting the attack of all acid fixing baths and their vapors has been realized by incorporating a sufficient but small percentage of molybdenum in the 18-8 or similar variety of stainless steel to produce Type 316 (molybdenum 2.0 — 3.0%),⁴³ the alloy with the higher molybdenum content being the most resistant. This alloy is classified here as highly resistant and the principal alloy of Group HR. Stainless Steel Type 317 is less extensively used but is also a member of this group. The relative cost of steels such as Type 316, however, is somewhat higher (35 to

§ When obtainable, this alloy with specification of a molybdenum content of 2.5 to 3.0% is more desirable. A grade known as Type TS316 contains molybdenum only 1.75-2.5% and should be reserved for only moderately severe usage such as with developers, plain acetic acid stop baths, acid fixing baths (but not chrome alum or rapid fixing baths), and washing equipment.

Fig. 2. Corrosion with Perforation, of Type 316 Molybdenum Stainless Steel by Air-Agitated Ferricyanide-Bromide Bleach.



50%) than the 18-8 Type 304 Stainless Steel, but the molybdenum addition provides ample resistance of the alloy to the sulfur dioxide present both in and above the solutions and prevents pitting under such conditions, which frequently causes failure of the Group MR alloys. These molybdenum stainless steels, therefore, are preferable for the construction of tanks, supply systems, and equipment for continuous use and where sulfur dioxide-laden vapors may be confined indefinitely; also for use with chrome alum stop baths and all rapid fixing baths.

In spite of the corrosion resistance of Type 316 to the vapor phase over acid fixing baths, this alloy is attacked and even perforated by the action of air-agitated plain ferricyanide-bromide bleach at room temperature, as shown in Figure 2. Under these conditions or without agitation, corrosion of the molybdenum-containing stainless alloy was not less than that obtained with the non-molybdenum Type 304.*

The most highly corrosion-resistant class of alloys is that comprising Group XHR.† These are principally complex alloys of either high chromium-nickel-molybdenum varieties or extremely hard cast-cobalt base alloys containing chromium and either tungsten or molybdenum.‡ They resist acid fixing baths and appear likely to withstand the action of highly acid oxidizing bleaches and other special strong acid solutions.§ Has-

* Some proprietary ferricyanide-containing bleaches for color products are recommended by the manufacturer for use in stainless-steel equipment, but with storage in non-metal vessels.

† Such as the following: Carpenter 20 (The Carpenter Steel Co., Reading, Pa.); Chlorimet 2, Chlorimet 3, Durco D-10, Durimet 20 and Durimet T (Duriron Co., Dayton 3, Ohio); Hastelloy C, various "Haynes-Stellite" Alloys (Haynes-Stellite Co., Kokomo, Ind.); Illium G (Burgess-Parr Co., Freeport, Ill.); Worthite (Worthington Pump & Machinery Corp., Harrison, N. J.).

telloy C alloy resists the action of plain ferricyanide-bromide bleach. Many of these alloys are available only in cast form and require special machining (grinding) and fabrication techniques because of their hardness. Intricate precision casting of the Hastelloy C and Hastelloy D as well as for other hard and resistant alloys is now available.†

(3) *Clad or Laminated Metals.* Several types of laminated or clad metals are available,^{44,45} which consist of a thin sheet of corrosion-resistant metal on one or both sides of a thicker metal base such as steel. For example, lead, nickel, Inconel alloy, silver, and various stainless steels have been integrally welded onto steel or iron in manufacture. Such materials are sometimes less expensive and more readily obtainable than the solid alloys, and it is possible that they will find some uses in photographic processing work. Certain precautions in selection and fabrication, however, should be emphasized. Careful selection of these materials must be made with reference to the suitability of the cladding metal for the intended use and the thickness of cladding. Special joining and welding precautions⁴⁶ are also necessary to avoid exposure of the base metal and to prevent inhomogeneities and dilution with the iron base metal at the joints, each of which may lead to attack. The steel exterior of laminated metal vessels should be protected from corrosive attack by the use of suitable organic protective coatings unless the steel is clad on both sides.

(4) *Plated Metals.* In view of the utility, cheapness, and availability of stainless alloys, plated metals are of little importance in photographic processing. Plated metals and alloys are always open to the objection that as soon as some of the plating wears off, exposing the other metal underneath, electrolytic corrosion sets in, and disintegration takes place rapidly. Such effects are apt to occur when the thickness of the protective layer is less than about 0.002 inch. Porous plating is also not uncommon unless considerable care is used.

Attention has already been called to the possible fogging action of zinc from the formation of sodium hydro-



Fig. 3. Roller Rod of 18-8 Stainless Steel, Type 303, Corroded by Ferricyanide-Bromide Bleach.

‡ Haynes-Stellite Co., Kokomo, Ind.; also The International Nickel Co., 67 Wall Street, New York 5, N. Y.

sulfite when the galvanized coatings of pails, etc., are in contact with bisulfites or acid solutions of sulfites during the preparation of developers.

An instance of the utility of plated metals in photography is the use of chromium-plated sheets and drums for ferrotyping glossy prints. In this connection it is important that the coatings be as free from pores as possible and also that the base metal be suitable. Zinc has been observed to be an unsatisfactory base metal since large diffuse black spots of silver were produced in the clear portions of prints. The spots were identified as resulting from electrolytic action from microscopic pores and scratches in the plating. Under the same conditions, chromium-plated copper or chromium on copper-plated steel did not show this behavior. Nickel is frequently plated on the copper before plating with chromium.

(5) Metal and Alloy Materials Generally Unsuitable in Given solutions.

Developers. In general, it may be stated that the following metals and alloys are unsuitable in developers or for containers for preparing developers because of fogging or staining effects:

- Aluminum
- Brass
- Bronze
- Copper
- Galvanized Iron or Steel
- Tin Alloys (Solders)
- Magnesium
- Soft Solder
- Tin
- Zinc
- Iron or Steel (with air present)

Acid Rinse and Acid Fixing Baths. The following metals and alloys are generally undesirable for continuous service in acid solutions such as acid rinse baths and acid fixing baths:

- Aluminum and its alloys
- Cadmium
- Copper
- Brasses and Bronzes
- Galvanized Iron or Steel
- Iron or Steel
- Lead
- Magnesium and its alloys
- Monel Alloy
- Nickel
- Nickel Silver (German Silver)
- Ni-Resist Alloy
- Stainless Steel of less than 18% Chromium, 7% Nickel
- Tinned Iron or Steel
- Zinc

Ferricyanide Bleach. The following metals and alloys are generally undesirable for continuous service in ferricyanide containing bleach solutions:

- Aluminum and its alloys
- Galvanized Iron or Steel
- Iron or Steel
- Magnesium and its alloys
- Monel Alloy
- Nickel
- Nickel Silver (German Silver)
- Ni-Resist Alloy
- Stainless Steels
- Tinned Iron or Steel
- Zinc

Figure 3 illustrates a processing machine roller rod of 18-8 stainless steel Type 303 deeply corroded by ferri-

cyanide-bromide bleach. This type of attack was avoided by the substitution of a similar roller of Hastelloy C alloy (see discussion of alloy classification XHR on page 84).

Bichromate Bleach. The following metals and alloys are generally undesirable for continuous service in bichromate-sulfuric acid bleach solutions as used in black-and-white reversal processing:

- Aluminum and its alloys
- Copper
- Brasses and Bronzes
- Galvanized Iron or Steel
- Iron or Steel
- Magnesium and its alloys
- Monel Alloy
- Nickel
- Nickel Silver (German Silver)
- Ni-Resist Alloy
- Tinned Iron or Steel
- Zinc

VITREOUS-COATED METAL

Vitreous-Coated Metal. Corrosion-resistant fused enamel coatings with few exceptions are seldom applied to the metal prior to fabrication. Rather, the vessels or equipment of steel or other non-resistant material are coated after forming or joining. Vitreous enamel and glass enamel-coated steel vessels and pipe are well known.

Enameled Steel. Enameled steel is used extensively in the form of relatively inexpensive small trays* and tanks* and has proved fairly satisfactory where it is not subjected to excessive mechanical shock or stress. When the undercoating of steel is laid bare by the chipping away of the relatively brittle vitreous enamel, it corrodes very rapidly, as with ferricyanide bleaches or toning baths, and the vessel and often the solution as well are rendered useless. Smooth, hard enamel coatings are resistant to weak acids used in photographic practice but with developers and alkaline solutions the surface becomes etched, making it difficult to clean. Dye solutions permanently discolor such roughened surfaces of enamel.

Vitreous enamels have, however, been greatly improved in recent years. Lower fusion point enamels have also been applied to aluminum⁴⁶ but are as yet untried for photographic use and chemical resistance.

Glass-Enameled and Glass-Lined Steel. Equipment having very satisfactory resistance to most photographic solutions (except strongly alkaline developers) is available in the form of mixing tanks and agitators (5 gallons upwards) suitable for motion-picture laboratory use.[†] Such equipment is made by fusing resistive silicate enamels onto substantial steel shells at a temperature of about 980 C (1800 F).^{46, 47} Advantages claimed are less weight and bulk and greater heat conductivity than with cast metals or earthenware. The glass enamel on the steel is much more resistant to breakage than ordinary enamel since it may have a relatively low coefficient of expansion, increased resistance to shock, and also be well fused onto the metal. Repairs in the event of breakage, however, are difficult to make without returning the entire unit to the factory. Recent developments in glass-

* By Columbian Enameling & Stamping Co., Inc., Terre Haute, Ind.
† By Pfaunder Co., Rochester 3, N. Y.

lined pipe permitting coupling with special corrosion-resistant threaded metal connections and other coupling innovations have been described by Orr.⁴⁸ These permit assembly and repair of glass-lined pipe in the field.

The concluding part of this paper, dealing with non-metal materials and practical suggestions for fabricating and maintaining photographic processing equipment, will appear in the next (August 1953) issue.

Ed.

References

1. Muchler, L. E., and Crabtree, J. I., "The Relative Corrosion Effect on Stainless Steels of Rapid Fixing Baths Containing Ammonium Chloride and Ammonium Sulfate," *Phot. Soc. Amer. J.*, Vol. 13, pp. 30-33 (1947).
2. *Metals Handbook*, T. Lyman, editor, American Society for Metals, Cleveland 3, Ohio, 1948.
3. *The Corrosion Handbook*, H. H. Uhlig, editor, John Wiley & Sons, Inc., New York, N. Y., 1948.
4. "Chemical Engineering Materials of Construction," *Ind. Eng. Chem.*, Vol. 39, pp. 1193-1264 (1947); Vol. 40, pp. 1773-1937 (1948); Vol. 41, pp. 2091-2154 (1949); Vol. 42, pp. 1951-2076 (1950); Vol. 43, pp. 2193-2294 (1951); Vol. 44, pp. 2285-2380 (1952).
5. *Chem. Eng.*, Vol. 53, pp. 110-150 (Nov. 1946); Vol. 55, pp. 116-128 (Nov. 1948); Vol. 57, pp. 107-154 (Nov. 1950).
6. *Machine Design*, Vol. 22, pp. 251-336 (Oct. 1950).
7. *Thomas's Register of American Manufacturers*, 42nd edition, Vols. I-IV, Thomas Publishing Co., 461 Eighth Ave., New York, N. Y., 1952.
8. *The International Nickel Co., Development and Research Division*, 67 Wall Street, New York 5, N. Y.
9. *Chemical Engineering Catalogue 1951-1952*, 36th edition, Reinhold Publishing Corp., New York 18, N. Y., 1951.
10. *Chemical Engineers' Handbook*, J. H. Perry, editor, 3rd edition, McGraw-Hill Book Co., New York, N. Y., 1950.
11. *Vilbrandt, F. C., "Chemical Engineering Plant Design,"* 3rd edition, McGraw-Hill Book Co., New York, N. Y., 1949.
12. *Riegel, E. L., "Chemical Machinery,"* Reinhold Publishing Corp., New York, N. Y., 1944.
13. "A.S.T.M. Standards 1952" (published triennially), American Society for Testing Materials, Philadelphia 3, Pa.
14. "A.S.T.M. Proceedings" (published annually), American Society for Testing Materials, Philadelphia 3, Pa.
15. "Modern Plastics Encyclopedia and Engineers' Handbook" (published annually), Plastics Catalogue Publications, New York 17, N. Y.
16. *Simonds, H. R., Weith, A. J., and Bigelow, M. H., "Handbook of Plastics,"* 2nd edition, D. Van Nostrand Co., New York, N. Y., 1948.
17. *Wakeman, R. L., "The Chemistry of Commercial Plastics,"* Reinhold Publishing Corp., New York, N. Y., 1947.
18. *Welding Handbook*, 3rd edition, American Welding Society, New York, N. Y., 1950.
19. *Latimer, W. M., "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions,"* 2nd edition, Prentice-Hall, Inc., New York, N. Y., 1952. The signs of potentials have been changed in accordance with present practice in corrosion literature. The values are those given in molal solutions (acid condition).
20. For further explanation, see the treatise of reference 18, and the publication "Corrosion (Processes—Factors—Testing)," The International Nickel Co., Inc., 67 Wall St., New York, N. Y., 1951.
21. *LaQue, F. L., and Cox, G. L., Trans. A.S.T.M.*, Vol. 40, pp. 670-89 (1940); see also "Corrosion (Processes—Factors—Testing)," reprinted from Nickel and Nickel Alloys, The International Nickel Co., Inc., 67 Wall Street, New York, N. Y., 1951, p. 17.
22. "Relative Corrodibility of Metals and Alloys" (Table), compiled by R. S. Burpo, Jr., from data obtained from publications of The International Nickel Co., Inc., and Westinghouse Electric Corp., Materials and Methods, Vol. 24, p. 1501 (1946).
23. Similar tests with somewhat more explicit instructions are given in Proposed American Standard "Tests for Determining the Chemical Resistivity for Photographic Inertness of Constructional Materials for Processing Equipment—PH4.13," in preparation. American Standards Association, Inc., 70 East Forty-fifth Street, New York 17, N. Y.
24. *Searle, H. E., and LaQue, F. L., "Corrosion Testing Methods,"* Proc. Amer. Soc. Testing Materials, Vol. 35, pp. 249-260 (1935).
25. *Amer. Soc. Testing Materials Standards 1949, Part I*, pp. 865-873, A.S.T.M. Designation: A224-46, "Recommended Practice for Conducting Plant Corrosion Tests."
26. *Amer. Soc. Testing Materials Standards 1949, Part I*, pp. 878-886, A.S.T.M. Designation: A279-44T, "Tentative Method of Total Immersion Tests for Stainless Steels."
27. *Champion, F. A., "Corrosion Testing Procedures,"* John Wiley & Sons, Inc., New York, 1952.
28. *Ross, J. F., and Crabtree, J. I., "The Fogging Properties of Developer Solutions Stored in Contact with Metals and Alloys,"* Amer. Phot., Vol. 23, pp. 254-264 (1929).
29. *Amer. Soc. Testing Materials Standards 1946, Part III-B*, A.S.T.M. Designation: D543-43, "Standard Method of Test for Resistance of Plastics to Chemical Reagents."
30. *Amer. Soc. Testing Materials Standards on Plastics*, Sponsored by A.S.T.M. Committee D-20 on Plastics, American Society for Testing Materials, Philadelphia 3, Pa., pp. 878-1076, June 1950.
31. *Crabtree, J. I., and Matthews, G. E., "The Resistivity of Various Materials Toward Photographic Solutions,"* Brit. J. Phot., Vol. 70, pp. 366-385 (1924); also *Ind. Eng. Chem.*, Vol. 15, pp. 666-671 (1923).
32. *Crabtree, J. I., Hartt, H. A., and Matthews, G. E., "The Effect of Electrolysis on the Rate of Corrosion of Metals in Photographic Solutions,"* Ind. Eng. Chem., Vol. 16, pp. 13-19 (1924).
33. *Crabtree, J. I., and Matthews, G. E., "Corrosion of Monel Metal in Photographic Solutions,"* Ind. Eng. Chem., Vol. 16, pp. 671-675 (1924).
34. *Ross, J. F., and Crabtree, J. I., "The Fogging Properties of Developer Solutions Stored in Contact with Metals and Alloys,"* Amer. Phot., Vol. 23, pp. 254-264 (1929).
35. *Addicks, L., "Silver in Industry,"* Reinhold Publishing Co., New York, N. Y., 1940.
36. *Uhlig, H. H., and Broughton, D. B., "Less Common Metals,"* Ind. Eng. Chem., Vol. 41, pp. 2153-2154 (1949); Broughton, D. B., *ibid.*, Vol. 42, pp. 2023-2025 (1950); *ibid.*, Vol. 43, pp. 2280-2282 (1951); *Yntema, L. F., and Bekebrede, W. R., ibid.*, Vol. 44, pp. 2364-2370 (1952).
37. "Comparison of Corrosion Properties of Zirconium, Titanium, Tantalum, Stellite No. 6, and Type 316 Stainless Steel," Materials and Methods, Vol. 35, pp. 115-117 (January 1952).
38. *Hutchinson, G. E., and Permar, P. H., "Corrosion Resistance of Commercially Pure Titanium,"* Corrosion, Vol. 5, pp. 319-325 (1949).
39. *Strauminis, M. E., and Chen, P. C., "The Corrosion of Titanium in Acids,"* Corrosion, Vol. 7, pp. 229-237 (1951).
40. *LaQue, F. L., "Inconel as a Material for Photographic Film Processing Apparatus,"* J. Soc. Mot. Pict. Eng., Vol. 24, pp. 357-371 (1935).
41. *Smith, H. A., "Newer Types of Stainless Steel and Their Application to Photographic Processing Equipment,"* J. Soc. Mot. Pict. Eng., Vol. 30, pp. 410-421 (1938).
42. *Everest, A. B., and Hudson, F., "Metals in Kinema and Related Equipment,"* Brit. Kinemat., Vol. 12, pp. 109-126 (April 1948).
43. "Seizing of Certain Metals at 750 F" (Table), from the data of Mochel, N. L., Materials and Methods, Vol. 26, pp. 111 (Sept. 1947).
44. *Woldman, N. E., "Nickel and High Nickel Alloys,"* Materials and Methods, Vol. 24, pp. 1475-1490 (Dec. 1946).
45. *Gosnell, E. C., "Corrosion-Resistant Processing Equipment of Clad Steels for Chemical and Allied Industries,"* Corrosion, Vol. 2, pp. 287-306 (1946).
46. "Clad Steels" (Materials and Methods Manual 30), Materials and Methods, Vol. 26, pp. 97-109 (Sept. 1947).
47. *Koenig, J. H., and Thomas, R. H., "Ceramics,"* Ind. Eng. Chem., Vol. 42, pp. 1961-1964 (1950); Koenig, J. H., and Snyder, N. H., *ibid.*, Vol. 43, pp. 2208-2217 (1951); Singer, F., *ibid.*, Vol. 44, pp. 2296-2308 (1952).
48. *Koenig, J. H., "Ceramics,"* Ind. Eng. Chem., Vol. 40, pp. 1782-1785 (1948); *ibid.*, Vol. 41, pp. 2102-2108 (1949).
49. *Orr, S. C., "Recent Developments in Glass Lined Pipe,"* Corrosion, Vol. 6, pp. 1-2 (April 1950).

PHOTOGRAPHIC SCIENCE AND TECHNIQUE

A quarterly technical supplement to PSA Journal

NATIONAL CONVENTION ISSUE — AUGUST 1953

HOW TO GET BETTER FIELD PHOTOGRAPHS	SHERMAN L. SMITH	91
MATERIALS OF CONSTRUCTION FOR PHOTOGRAPHIC PROCESSING EQUIPMENT, (CONCLUDED)	L. E. MUEHLER AND J. I. CRABTREE	92
PRODUCTION OF PHOTOGRAPHIC GELATIN	JOSEPH H. COHEN	105
KINETICS OF DEVELOPMENT OF LIQUID PHOTOGRAPHIC EMULSIONS III. DEVELOPMENT BY N-METHYL-P-AMINOPHENOL (METOL)	L. J. FORTMILLER AND T. H. JAMES	109
LIGHT-BALANCING FILTERS FOR COLOR PHOTOGRAPHY	L. D. CLARK	112
BETTER PHOTOGRAPHIC LENSES FOR THE SIGNAL CORPS	JOHN C. THOMAS, JR., AND CARROLL W. ARFORD	118
PHOTOGRAPHY IN OPHTHALMOLOGY	DAN M. GORDON	121
PURPOSES OF PHOTOGRAPHY IN THE GENERAL BIOLOGICAL SCIENCES	WAYNE M. HULL	122
COLD-CATHODE LIGHT SOURCE POTENTIALS IN PHOTOGRAPHY	DAVID B. EISENDRATH, JR.	125
THE DEPTH OF FOCUS AND DEPTH OF FIELD OF PHOTOGRAPHIC OBJECTIVES	JOHN D. HAYES	128
PROPERTIES OF DEVELOPING AGENTS. III. COMBINATIONS OF AMINOPHENOLS AND HYDROQUINONES	R. W. HENN	131



WE NEVER HAD IT SO GOOD

Fifteen years ago amateur photographers, and some professionals, showed excessive interest in film speed ratings. They had the same avid curiosity about the latest "Weston number" for a certain film that investors showed in the market closing figure for a favorite stock.

A speed rating, in those days, appeared to be the prime criterion of film quality. Speed numbers received a great deal more attention than was paid to color sensitivity, gradation characteristics, graininess, latitude, or other qualities essential to good photography.

With the approval in 1943 of American Standard Method for Determining Photographic Speed and Speed Number, speed ratings were deemphasized. Interest in frequent publication of speed ratings with hair-splitting variations diminished.

The authoritative voice of the American Standards Association did much to calm this fevered situation. Photographers themselves by 1943, however, had begun to come to their senses. It was realized that the difference between "Weston numbers" 50 and 64 (only one-third of a lens stop) was of no practical significance while a camera lens or shutter was graduated no finer than half-stop intervals.

The American Standard of 1943 was revised in 1946 and again in 1947 when the title was changed to emphasize the term *EXPOSURE INDEX*. Also in 1947 a substantially identical standard was adopted in Great Britain. In 1848 the American Standard was circulated to the members of Technical Committee 42 on Photography of the International Organization for Standardization. The ISO balloted in 1951 to approve the ASA method as an *INTERNATIONAL STANDARD PROPOSAL*. The outcome of that ballot comes before the ISO for action at its annual meeting in Switzerland this summer.

The British-American accord and the circulation of the international standard proposal could have brought to other countries the benefits enjoyed in North America. The old speed rating chaos and confusion could have been replaced abroad by a situation of stability, unity, and confidence in standard film speed ratings. Reports from overseas, however, indicate that progress is rather slow.

A large share of the blame for the film speed chaos overseas lies at the door of the European exposure meter

manufacturers. The following list, taken from an instruction sheet for a British made film, shows how widely different in calibration (by design) various exposure meters currently available in England are for the same film.

SPEED SETTING (DAYLIGHT) FOR PHOTO-ELECTRIC EXPOSURE METERS

Avo	400 H. & D.	Metrovick	20° Scheiner
Avo Model I	19°	Obmrus	20° Scheiner
Avo-Smethurst		Photoscop	17° Scheiner
Highlight		Practos II	400 H. & D.
Blendux	18° Scheiner	Prinsen	26° Scheiner
Chum	17° Scheiner		400 H. & D.
DeJur	8 A.S.A.	Prix meter	20° Scheiner
Dornlei	17° Scheiner	Pullin	B.S.I. 6
Electro Bewi	17° Scheiner	Rex	19° Scheiner
	13/10 DIN	Novo-Rex I	22° Scheiner
Electrodrem	20°-22° Scheiner	Sixtus	20° Scheiner
Eos	20° Scheiner		9/10 DIN
Excelsior	23° Scheiner	Tempiphot	19° Scheiner
G. E. (U. S. A.)	8 A.S.A.	Weston Leica	
G.E.C.	23° Scheiner	Meter	17° Scheiner
Helios	23° Scheiner	Weston Meters	6 Weston
Ilford	Group C	Zeiss Helicon	18° Scheiner

European exposure meter manufacturers are not the only ones at fault, according to the British Journal of Photography. An editorial in the 1 May 1953 issue complains about the failure of British film manufacturers to use the standard they unanimously agreed in 1947 to adopt.

By publishing speed ratings for obsolete systems and for meters with non-standard calibration, a film manufacturer allows the tail to wag the dog. American film manufacturers have adhered to American Standard Z38.2.1 and have steadfastly refused to publish film sensitivity ratings in terms other than the American Standard *Exposure Index*. When photographic film manufacturers abroad adopt a similar policy, the photographic public which they serve will begin to enjoy the benefits of standardization that are implicit in British Standard 1380.

National standards, of course, have no police force behind them in the free countries. They are sound declarations of agreement that a certain method, procedure, or value is the best one for all to follow. They

THIRD 1953 ISSUE ☆ VOLUME 19B, NUMBER THREE ☆ PUBLISHED WITH THE PSA JOURNAL FOR AUGUST 1953

PHOTOGRAPHIC SCIENCE AND TECHNIQUE BOARD OF EDITORS

EDITOR, PAUL ARNOLD, APSA
26 Hotchkiss Street, South Binghamton, N. Y.

LAWRENCE B. FRAIR P.O. Box 1009 Rochester 3, New York

MORRIS GURRIE 3412 N. Bernard Street Chicago 25, Illinois
R. C. HAKANSON 10322 Lake Shore Boulevard Cleveland 8, Ohio
HUTSON HOWELL 700 Commonwealth Avenue Boston, Massachusetts

PETER KRAUSE, APSA 69 Bourndale Road, South Manhasset, New York
HERBERT MEYER 1421 Northwestern Avenue Hollywood 27, Calif.
JOHN B. TAYLOR 118 Laurel Avenue Binghamton, New York

PHOTOGRAPHIC SCIENCE AND TECHNIQUE is an official organ of the Photographic Society of America dedicated to the publication of scientific and technical papers dealing with the theory and practice of photography. Its aim is to encourage the publication of authoritative articles describing original research, techniques, and the engineering aspects of new equipment in all fields of photography. It is intended to interest and inform the advanced amateurs, the professionals, the technologists, and the scientists who study or apply photographic processes.

Prepared four times yearly by the Technical Division, Photographic Science and Technique is published as SECTION B of the PSA JOURNAL. The issues are separately numbered and page numbered and indexed annually.

Society memberships, including subscriptions to both publications, may be obtained from PSA Headquarters, 2005 Walnut Street, Philadelphia 3, Pennsylvania, upon payment of \$10.00 annual dues. Separate subscriptions are not available, except institutional and library subscriptions at \$5.00 a year. No extra charge is made for mailing to foreign countries.

ASST. EDITOR, H. LOU GIBON, FPSA
343 State Street Rochester 4, New York

Address all manuscripts and communications to the Editor. Unacceptable manuscripts will be returned promptly. No responsibility is assumed for the accuracy of statements by contributors but attempts will be made to avoid the publication of errors. The contents will be protected by domestic and foreign copyright and may not be reproduced without the written permission of the editor. The publishing of opinions expressed by authors does not necessarily indicate concurrence or endorsement by the editors, by the Technical Division, or by the Photographic Society of America.

rely for adoption on voluntary acceptance of democratic principles plus a self-interested recognition of the compensations—economic and moral—of being in step rather than out of step with one's contemporaries.

American photographers, safe in the enjoyment of standard film Exposure Indexes and reliable photoelectric exposure meters calibrated in accordance with American Standards, look back without regret on their own confusion of fifteen years ago.

American film manufacturers, with film speed relegated to its proper importance as a quality characteristic through unanimous, voluntary publication of nothing but American Standard ratings, may marvel at their British cousins with their self-inflicted woes.

American photographic dealers, who remember the previous turmoil before film exposure indexes were standardized in this country, must contemplate the present state of affairs and reflect *we never had it so good!*

HOW TO GET BETTER FIELD PHOTOGRAPHS

Sherman L. Smith*

Photographs taken in customers' plants in various parts of the country can be a real headache to the advertising manager. If the salesman is merely asked to hire a photographer and get a picture of the product in use, he is confronted with a job totally unfamiliar to him. He doesn't know how to go about it. He is afraid of it. He will put it off as long as he can. If and when he does the job, the results are likely to be unsatisfactory.

The Bostitch advertising department furnishes a list of eleven instructions to guide the salesman in taking these photographs, after he has obtained permission from his customer.

1. *Employ a competent commercial photographer.* Some photographs cannot be used for reproduction because they are poorly lighted, improperly focused, or show the subject from unsatisfactory viewing angles. Money spent for inferior photographs is wasted, no matter who takes them.

It is surprisingly difficult to find good commercial photographers in some cities, even large ones. A photographer who can sense, after satisfactorily completing a few job assignments, what the customer wants so that thereafter he can be sent out on assignments alone, is a rare individual. The inferior quality of work turned out by some established commercial photographers is really amazing. There are good ones, however, that can be found if one looks long enough.

2. *Furnish 8 × 10 inch glossy prints.* Pictures taken with smaller cameras should be enlarged to 8 × 10 inch size. Most advertising illustrations require retouching and this size enables the retoucher to do a good job.

3. *People should look natural.* The subjects should never be photographed looking at the camera but should have their eyes on their work. Hands should be in normal working position unless changes are required to avoid hiding something important to the story.

People have to be handled carefully. Most women operators (and some men) if they know in advance that pictures are to be taken, will doll up like movie stars and try to pose accordingly. It is usually helpful first to ask the model for his name and address and to promise him a print of the picture.

4. *Select good looking operators for models* whenever this can be accomplished tactfully. There is a limit to what retouching can do.

5. *Competitive products should not show* anywhere in the picture.

6. *Surroundings should look natural.* A little straightening and picking-up is helpful but the scene should not be "prettied up" so that it looks too neat for a work place.

* Advertising Manager, Bostitch, Westerly, R. I. Adapted from an article in *Printer's Ink* for March 6, 1953.

7. *Make all possible preparations before asking the operators to stop work.*

8. *Check the image on the ground glass.* The photographer probably knows more about taking pictures than you do, but you know more than he does about what is wanted in the picture.

9. *Ask the photographer to deliver the negatives with the prints.* It is unlikely that additional prints will be needed, so the photographer will probably not lose additional print sales. Photographers often are reluctant to give up the negatives. In such cases, purchase a duplicate print of each picture to keep in our files, just in case.

10. *Keep yourself out of the picture.* Occasionally a picture is spoiled for advertising use because a salesman can be seen hovering in the background. The temptation to appear in a national advertisement should be squelched by the realization that, even if he appears in the photograph, the salesman will not appear in the ad. The retoucher usually can take him out, at a price.

11. *Get a signed release when a close-up of an operator is shown* for which you pay the operator one dollar. Releases should be obtained even when the model, in a spirit of generosity, wishes to decline payment. Such situations usually can be handled by saying: "My company requires me to turn in a release or they won't accept the picture." An operator generous enough to decline payment will usually be considerate enough not to put the photographer or the salesman on the spot.

The release form must be as simple as possible while meeting legal requirements. A release that looks formidable will scare some people out of signing. For this reason we use a simple mimeographed form which reads as follows:

For value received, I hereby consent to the use for advertising or trade purposes of the originals or reproductions of the photographs of myself taken on
at ... (company name) by
or by any of its customers or other interested parties without limitation or reservation.
City..... Date.....
Signature.....
Witness.....

We find it most tactful to present the release form and the dollar *after* the picture taking is all over. This precludes forming the impression that the consideration is a model fee. Should a model fee be necessary or desirable, the amount would be considerably more.

MATERIALS OF CONSTRUCTION FOR PHOTOGRAPHIC PROCESSING EQUIPMENT*

L. E. Muehler and J. I. Crabtree

SUMMARY

Various types of non-metal materials from the wide field available are discussed in relation to certain properties and uses in photographic processing equipment. The substances range from natural materials such as quarried silicate rock (Alberene stone) and wood to a host of synthetic products, including ceramic and glass compositions, rubber and synthetic elastomer materials, plastics, and organic coatings and linings. Relatively thin organic coatings are not recommended for continuous service. The fact that modified wood products, such as paraffined wood and thermosetting phenolic resin-bonded plywood, are waterproof makes them useful in certain cases. The desirability is stressed of selecting a material and knowing its general characteristics prior to the detailed designing of processing equipment. Materials can be selected from the summary tables or determined by separate chemical resistivity and photographic inertness tests as previously described. Approved methods of fabricating tanks of stainless steel are described, the metallic arc method being preferred, using water-cooling applied to the back as the welding proceeds except with stabilized or extra low carbon varieties. Some peculiarities and cautions in regard to stainless steels, their properties, use, and care are emphasized. Methods of spot-testing metals and alloys for identification are discussed, and a rapid method of differentiating Type 316 and other molybdenum-containing stainless steels from the non-molybdenum varieties is given.

NON-METAL MATERIALS, organic coatings, and linings may be considered together and are listed as follows:

- A. Alberene Stone
- B. Asphalt-Rubber Compositions
- C. Carbon and Graphite Compositions
- D. Cement and Concrete
- E. Chemical Stoneware
- F. Glass
- G. Rubber and Synthetic Elastomer Materials
- H. Plastics (General)
 - 1. Synthetic Thermoplastic Resins and Plastics
 - 2. Synthetic Thermosetting Resins and Plastics
- I. Organic Coatings and Linings
- J. Wood, Paraffined Wood, and Resin-Bonded Plywood

Many non-metal materials are now available that have the advantage of relatively high chemical resistance, but selection must be properly made. As a class, the non-metals have poor heat-transfer characteristics. Glass, ceramics, and chemical stoneware are hard, generally brittle, and subject to breakage due to strain or impact. Synthetic elastomer materials of superior chemical resistance are gradually replacing natural rubber. Thermoplastics exhibit cold flow and distortion at appreciably elevated temperature (depending upon the softening point of the particular material). Organic coatings are available in a wide variety but are generally useful for temporary rather than continuous protection of metal surfaces. Thicker organic coatings and linings are more appropriate for continuous service. Wood, formerly used because of its cheapness, availability, or ease of working, is being displaced in some instances by laminated wood and resin-bonded plywood products, and in model construction by plastics because of convenience in forming and joining with appropriate solvent cements.

* Concluded from Volume 19B, Number 2, pp. 79-88, May 1953.

A. Alberene Stone

Alberene stone,[†] a dark gray natural quarried silicate rock soapstone material is useful for sinks, drainboards, laboratory bench tops, and large developing, fixing, rinsing, and washing tanks but is being displaced for most of these purposes by stainless steel. In selecting Alberene stone, care should be used to obtain a grade having a dense fine crystalline structure, otherwise spalling will result from crystallization of the sodium thiosulfate constituent of fixing baths and also from crystallization of developers above the air-line of the solution. Grade 25 is specified for photographic use in view of the work of the National Bureau of Standards.^{49, 50} Sinks and tanks of Alberene stone should not be subjected to temperatures of 125 F or higher for long periods, nor to extreme and rapid changes in temperature, since cracks which allow leakage will result.

B. Asphalt-Rubber Compositions

Asphalt compositions, when used alone or in combination with a minimum amount of hard rubber, as in some so-called hard-rubber composition tanks either with or without a mineral filler, are usually not satisfactory as materials for photographic containers. The vessels warp readily with heat and the surfaces in contact with developers may disintegrate rapidly. Depression of image development of sensitive emulsions (loss of photographic speed) has also been found in some instances when developers have been stored in certain asphalt-rubber composition tanks.

C. Carbon and Graphite Compositions

Carbon and graphite compositions which are highly corrosion-resistant are available in pipe, pipe fittings, valves, and other forms.[‡] These have many possible

[†] Alberene Stone Corporation of Virginia, 419 Fourth Ave., New York, N. Y.

[‡] National Carbon Co., Inc., 30 East 42nd St., New York 17, N. Y.

applications, although experience with their use for photographic baths as yet is not very extensive. These materials are brittle like hard rubber and many non-reinforced resins. However, some types can be threaded with standard pipe tools. Rope wrenches should be used in assembling, and care in sawing or shaping must be exercised to avoid thin sections and to locate or shield the part suitably from mechanical abuse.^{61, 62, 63} Carbon-graphite* mechanical parts as for bearings, rings, seals, disks, etc., which are press-molded and baked at 3000 F stand up under extremes of speed, temperature, and chemical exposure. In a published account of such parts, 143 chemicals are listed which do not react with or affect them.⁶⁴

D. Cement and Concrete

Tanks made of reinforced concrete faced with cement have been used to some extent by photofinishers for wash tanks and in a few cases for developer tanks. They are generally unsatisfactory for use as fixing baths because of the tendency toward disintegration when the hypo crystallizes in the pores of the cement. Steel reinforcement is necessary for all sizes of concrete tanks. The surface preferably should be treated with several coats of a corrosion-resistant paint suitable for concrete, such as Parlon chlorinated rubber paint,⁶⁵ or with a hard (air-blown) asphalt, the latter being applied with the aid of a blowtorch and smoothed with a hot iron.

When large tanks are installed, the floor load should be checked carefully and the tank set on concrete beams to raise it off the floor and permit easy cleaning around and under the tank. The upper edges of a concrete tank should be protected with a cypress wood facing to prevent chipping. For a proper waterproof treatment and construction of concrete floors and floor foundations for heavy tanks and drains, see illustrations and discussion in a useful treatise.⁶⁶

E. Chemical Stoneware

Tanks of high-grade, dark-brown earthenware, glazed on both sides and designated by manufacturers† under the general term "chemical stoneware"^{67, 68, 69} have been found generally servicable in small and even in large installations for the storage of developing and fixing solutions. They should not, however, be used with strong alkali (caustic-containing) solutions. A form of hard, glazed chemical stoneware was introduced in 1933 which was claimed to be free from internal fissures, and to be lighter and thinner than the older types but equally strong and chemically resistant.

In recent years chemical stoneware for tanks and other vessels has been largely replaced by stainless steels and stainless alloys. Ceramic chemical pipe remains very satisfactory for ultimate chemical drainage from Duriron alloy or Ni-Resist alloy building drain lines. The rate of heat transfer from ceramic and chemical stoneware materials is low compared with that of metals. The possibility of breakage and the difficulty of working or repair may account for the decreasing use of chemical stoneware tanks.

F. Glass

In general, glass is relatively inert in all solutions in photography except those containing strong alkalis. For storage of strong alkalis, special resistant glass⁶⁰ should be used, otherwise the amount of insoluble silicate material formed may be objectionable.

One of the most useful glasses from an engineering standpoint is borosilicate 774 glass.⁶¹ This is a member of the so-called "heat-resistant" type of glasses, of which Pyrex‡ glass is an example. This glass of low thermal expansion is employed for chemical apparatus, sintered filters, chemical piping, centrifugal pumps, and even for filter cloth and heat insulation. It is available in plate up to about 1/2-inch thickness in sizes up to somewhat less than 24 X 30 inches.⁶² Fibrous glass material, an example of which is Fiberglas,§ is used for filter cloth,⁶³ heat insulation, and for reinforcing plastics.

Methods of fabricating glass apparatus have advanced, for example, improvements in the technique of forming all-glass tanks from shock- and heat-resistant Pyrex glass plate by special edge-fusion methods, and high-temperature electrical conduction methods of welding Pyrex glass piping.^{61, 64, 65} With Pyrex glass piping, it is no longer necessary, for most purposes, to join the ends by fusion. Rather, the slightly flared ends are drawn together with special metal, bolted connectors which are lined with hard asbestos, rubber, or Teflon (polytetrafluoroethylene) where they contact and gasket the butt ends, and exert pressure on the flared shoulders.⁶¹ Working pressures for glass piping from 1 to 3 inches in diameter should not exceed 50 pounds per square inch; lower pressures should be used for larger diameters.⁶⁶

In designing and making installations of Vitrolite plate glass for bench and table tops, the mounting should be made on a resilient, load-spreading pad, and concentrated loading of the surface at any time or during use should be avoided. Also, high-heat devices (ovens, incubators, electric hot plates, etc.) should not be placed on such bench or table tops.

G. Rubber and Synthetic Elastomer Materials

High-grade hard rubber withstands practically all photographic solutions at normal temperatures. It does have the disadvantage of deforming in hot water or warm solutions. As early as 1933, thermoplastics were introduced⁶⁷ which were made from acid or metallic salt cyclized or polymerized rubber. The products were said to be sulfur free, and to have greater hardness and less susceptibility than hard rubber to heat distortion in the usual processing range. Hard rubber is suitable for small tanks and trays to be used at approximately 65 to 75 F (18 to 24 C). It is also very satisfactory for custom- or manufacturer-installed linings, cemented and vulcanized in place in large and small metal tanks. Soft natural rubber is often not satisfactory for metal tank linings since it tends to crack and harden with time and exposure to sulfur dioxide, air, and fixing-bath chemicals. A three-ply construction of soft and hard rubber described by Fritz and Hoover^{68, 69} represents a desirable type of lining|| for metal tanks;⁷⁰ it withstands organic acids,

* United States Graphite Co., 1621 Holland Ave., Saginaw, Mich.

† United States Stoneware Co., Akron, Ohio; also General Ceramics and Steatite Corp., Keasbey, N. J.

‡ Corning Glass Works, Corning, N. Y.

§ Owens-Corning Fiberglas Corp., Toledo 1, Ohio.

|| B. F. Goodrich Co., Akron, Ohio.

salts, and alkali solutions for long periods at temperatures up to about 150 F (65 C).

Modern synthetic plastics and rubberlike elastomers of appropriate resistance to aqueous solutions of chemicals are now strong contenders for the photographic uses of hard rubber as well as soft rubber. A large-scale manufacturer of hard rubber now also produces a number of plastic products, including sheets, rods, and tubes of polyethylene, or Polythene resin, and also polyvinylidene chloride.⁷¹ For certain types of installations, hard rubber piping is very satisfactory because it is light and can be threaded easily. Its chief disadvantage is its brittleness. Less brittle rubber and styrene co-polymer materials such as Riji-Tuf* and Uscolite† are available in pipe and fittings. Iron pipe lined with hard rubber, integrally vulcanized to the metal, represents a very satisfactory type of piping since it does not require support every few feet and will not break on impact. Even in this field Saran polyvinylidene-chloride-lined iron pipe is equally satisfactory.

Cheap rubber products often contain an excess of free sulfur which reacts with photographic developers and causes chemical fog.⁷²

Other chemical compounds containing divalent sulfur in combined form as in sulfides, polysulfides, thiourea, or Captax mercaptobenzothiazole may be present in many rubber products, including cements, sheeting, and tubing, and by dissolving in developers produce either fog or depression of density or development, depending upon the nature of the compound. For this reason it is undesirable to allow artificial rubber materials made by the use of the polysulfides to come in contact with developers.

Some synthetic rubberlike elastic materials,⁷³ for example, Koroseal,‡ a polyvinyl chloride highly plastized derivative, and the chloroprene base neoprene§ elastomers^{74, 75} are superior to the products made from natural rubber in resistance to deterioration by oxidation (aging), oxidizing solutions, strongly corrosive acid and alkaline solutions, and sulfur dioxide. Neoprene elastomer is more like natural rubber in its physical properties than any of the other synthetic elastomers.⁷⁶ It can, however, be vulcanized by heat without the use of sulfur.⁷⁷ In flexible sheet form, these materials can be used for lining trays, troughs for reel processing, tanks, and for gaskets. They are also available in hose and tubing.

In rapid fixing baths which contain ammonium thiosulfate, some types of rubber have been found to exhibit undesirable swelling properties, even at ordinary room temperature (70 F). However, under the same conditions, Koroseal, neoprene, and flexible Tygon|| elastomers were not appreciably affected. In 3 per cent acetic acid, these synthetic elastomers were also satisfactory at room temperature over a period of several months, whereas some samples of ordinary rubber swelled excessively.

* American Hard Rubber Co., 93 Worth St., New York 13, N. Y.

† United States Rubber Co., 1232 Avenue of the Americas, New York, N. Y.

‡ B. F. Goodrich Co., Akron, Ohio.

§ E. I. du Pont de Nemours & Co., Inc., Organic Chemicals Dept. (Rubber Chemicals Division), Dept. R.T., Wilmington, Del.

|| The United States Stoneware Co., Akron 9, Ohio.

H. Plastics (General)

The term plastic, while applying to the molded or finished material or article, in general, refers to any synthetic (usually organic) material capable of being formed, or formed and set, by the use of heat. Thus, "thermoplastic" and "thermosetting" are two general types of plastics. The term resin, preceded by the chemical name or other designation, denotes the material itself or the finely divided material used for molding or for preparing solutions suitable for protective coatings on metal or other material. Generally speaking, all plastics are available in complex molded forms as well as in sheet, rod, tubing, and pipe. The variety and number of plastics are so great that reference should be made to previously cited treatises for more detailed listing and information.^{78, 79} Some types of plastics may be enumerated as follows:

- Acrylate Resins
- Cellulose Acetate-Butyrate
- Furan Resins
- Phenol-Formaldehyde Resins
- Resorcinol-Formaldehyde Resins
- Phenol-Furfural Resins
- Polyamide Resins
- Polyester Resins
- Polyethylene
- Polystyrene and Co-polymers
- Polytetrafluoroethylene
- Polymono-chlorotrifluoroethylene
- Silicone Resins
- Vinyl Polymers and Co-polymers
 - Polyvinyl Chloride Resins (unplasticized-rigid) (highly plasticized-flexible)
 - Polyvinyl Chloride-Acetate
 - Polyvinyl Acetal
 - Polyvinyl Butral
- Vinylidene Chloride Resins

An excellent comprehensive descriptive survey of the physical and chemical resistance properties of plastics with over 500 references has appeared.⁸⁰ Chemical and physical methods of identifying a plastic were published in 1948⁸¹ and 1950.⁸² A short section on some plastics in darkroom equipment appeared in 1949.⁸³ Some applications of modern plastics in chemical equipment and coatings stressing uses and limitations of the older as well as of some more recent materials have been discussed.⁸⁴ Comprehensive instructions were published on fabricating and finishing a variety of plastics,⁸⁵ including directions for cementing thermoplastics.⁸⁶ Lathe and tool conditions for turning thermoplastic and thermosetting plastics have also been given.⁸⁷

Synthetic Thermoplastic Resins and Plastics

Synthetic thermoplastic materials combined advantages in resistivity to attack and ease in fabrication for small apparatus and parts, as well as for small tanks and trays. Some of the materials have even been used as tank linings. Reinforced molded products have been made, utilizing inert Fiberglas fibers¶ and cloth, and likewise asbestos materials.

¶ Owens-Corning Fiberglas Corp., Toledo, Ohio.

As the term thermoplastic indicates, these materials become softened and are capable of being formed or molded when sufficiently heated. The softening process is repeatable. Thus, the molded part, when heated to a degree dependent upon the type of material is subject to deformation. The heat-distortion (softening) point is measured by the temperature where a particular thermoplastic begins to exhibit distortion appreciably with the application of a force which may be mechanical or, as a practical example, its own weight acting on a suspended length of the material.

The swelling properties of a given thermoplastic should be considered, particularly when an organic solvent is present in the processing solutions. Some color-forming developers contain organic solvents which may affect thermoplastic materials. Solutions containing dyes as used in dye toning sometimes color plastic materials. The slight, but possible action of caustic alkalis, as with Tenite II* cellulose acetate-butyrate or the functional but undesirable hydrolysis by mineral acids in the case of nylon†^{95, 99} should be taken into account when planning a material for a given use. In general, a high heat-distortion value is desirable, but such materials may become too brittle for satisfactory performance. Specific suggestions with respect to chemical resistivity are given subsequently in the Summary Tables of Materials and Use.

Trays and small vessels made of plastics having moderately high heat-distortion (softening) points, for example, methyl-methacrylate and polystyrene,‡ are useful in a wide range of photographic solutions and withstand temporary washing with moderately hot water (125–150 F). Thermoplastics with high heat-distortion points are sometimes brittle, but this is not necessarily true, since suitable plasticizers and modifiers may be present in the material. Some new polystyrene products include a small amount of synthetic rubber to improve their impact (and shatter) strength.⁹⁰ Special types of acrylates§ and of polystyrene|| plastic molding materials having ASTM heat-distortion points of 190 F and somewhat higher for applications requiring high-temperature service are claimed to withstand boiling water for limited or even extended periods, depending upon the material.

Plastics of acrylate type¶ and Tenite II** cellulose acetate-butyrate are resistant to many types of photographic solutions and have the advantage that they can be cut easily and joined by the use of the proper adhesives and

cements recommended for each material.⁹⁶ Such products are useful for the construction of small apparatus including trays, tanks, film hangers, automatic tray siphons for use in the washing of prints,⁹¹ and intricate processing devices. Tenite II is joined by the use of methods similar to those described for the earlier cellulose ester materials. The acrylate plastics, such as methyl-methacrylate, have shown considerable brittleness, as indicated by their lower impact strength, but they have the advantage of being glass-clear, with good dimensional stability, and are therefore useful in making narrow molded or cemented cells for demonstration purposes or exhaustion tests of solutions.

Ordinarily processed silver image photographic prints should not be stored in contact with plastics, such as methyl-methacrylate or other plastics which use peroxides as polymerization catalysts, since the images may become toned and faded.

Produced as tubing and in the form of fittings and piping⁹² of standard sizes to be assembled in various ways are processing solution-resistant materials, such as Tenite II* cellulose acetate butyrate, polyethylene,† polyvinylidene chloride,‡ and polyvinyl chloride.§ Of these, polyethylene is the softest and most yielding, having the low ASTM heat-distortion point of 107 F. Heat-distortion points of the other materials are given as follows: cellulose acetate butyrate, 120–210 F; polyvinylidene chloride, 150–180 F; and rigid polyvinyl chloride, 175 F. Since the pipes are thermoplastic, they are subject to distortion unless properly supported. They should also be kept away from highly heated locations.

Steel pipe is available with a lining of Saran|| polyvinylidene chloride, utilizing specially designed lined fittings which permit joining the threaded pipe, with no metal exposed to the solution.

Polyethylene is also useful in the form of nonbreakable flexible bottles, screw-cap bottle liners, and thin films or sheeting. Since polyethylene has a density slightly less than unity, thin sheets of thickness approximately 0.008–0.03 inch can be used as floating covers to protect photographic solutions, such as tray developers, against oxidation and evaporation, or to decrease loss of volatile ingredients from other solutions. An important consideration is that the sheeting be flat and no appreciable amount of water or solution be present on its upper side. The thinner material is perhaps best for the purpose. The sheeting is cut with a photographic trimmer or ordinary shears to a size only slightly smaller than the surface exposed by the solution.

For tank linings, finely divided or powdered poly-

* Tennessee Eastman Co., Kingsport, Tenn.

† E. I. du Pont de Nemours & Co., Inc., Polychemical Dept., Wilmington 98, Del.

‡ Bakelite Polystyrene, Bakelite Division, Union Carbide & Carbon Corp., New York 17, N. Y.

§ Styron, Dow Chemical Co., Midland, Mich.
Lustron, Monsanto Chemical Co., Plastics Division, Springfield, Mass.

|| Plexiglas V, Rohm & Haas Co., Philadelphia, Pa. See reference 78, 1948 edition, p. 144.

¶ Lustron, Monsanto Chemical Co., Plastics Division, Springfield, Mass. See reference 78, 1948 edition, p. 170.

|| Koppers Polystyrene P-8, Koppers Co., Inc., Pittsburgh, Pa. See reference 78, 1949 edition, p. 281; compare also p. 282–3.

¶ Lucite Manual, E. I. du Pont de Nemours & Co., Inc., Plastics Dept., Arlington, N. J.

Plexiglas Fabricating Manual, Rohm & Haas Co., Philadelphia, Pa.

** Tennessee Eastman Co., Kingsport, Tenn.

* For various firms producing Tenite II cellulose acetate butyrate and other plastic pipe and fittings, see reference 92.

† Polyethylene, American Hard Rubber Co., New York 13, N. Y.

‡ Polyethylene resin, Bakelite Division, Union Carbide & Carbon Corp., New York 17, N. Y.

§ Polythene resin, E. I. du Pont de Nemours & Co., Inc., Plastics Dept., Arlington, N. J.

|| Saran resin, Dow Chemical Co., Midland, Mich.

§ Tygon resin, United States Stoneware Co., Akron 9, Ohio.

Boltaron 6200 Series, based on B. F. Goodrich Geon 404 resin and produced by Bolta Products, Inc., for H. N. Hartwell and Son, Inc. (exclusive distributors), Boston, Mass.

|| Produced by the Dow Chemical Co. and distributed by Saran Lined Pipe Co., 2415 Burdette Ave., Ferndale 20, Mich.

ethylene can be used in a flame pistol* or flame torch,† and flame-sprayed onto well-prepared sand- or alumina-blasted metal surfaces to form quite adherent coatings. These are quite resistant to attack by most photographic solutions.

Some thermoplastics can be joined analogous to metal welding by appropriate cutting of the edges to be joined, using a plastic welding stick and heating or welding with electrically heated hot-air jet guns,‡ or hot-air torches.¶ Hydrogen and other gas-heated guns have also been used by plant fabricators because of lightness of weight, easy handling, and accessibility to the work, and high heat capacity when required. The welding operation with electrically heated hot air, while in most respects quite similar to the usual gas welding, or brazing of metals, is obviously not particularly hazardous. For example, the heat required for welding Boltaron 6200 Series is given as 375–390 F at an air-flow requirement of 35–50 cubic feet per hour. Among the plastics that may be cited, Tenite II cellulose acetate butyrate, polystyrene, polystyrene and co-polymers, rigid (unplasticized) polyvinyl chloride, Saran polyvinylidene chloride, and polyethylene can be heat-joined and hot-air jet-welded. As an instance of a versatile high impact-strength material in this class, rigid polyvinylchloride§ 96, 97 is resistant to all alkalis, acids, and oxidizing agents in the strengths used in photographic solutions and has been successfully used for bleach tanks and tank linings, welded tubing, flanged or standard threaded piping, and parts of various shapes where either machining or unavailability would make stainless steel or higher resistant alloys impractical. A heat-welded and -flanged pipe "T" of rigid polyvinylchloride is shown in Figure 4.

Teflon polytetrafluoroethylene|| is an unusually dense, tough, and chemical-resistant plastic produced by various plastic molders in limited sizes of sheets, rods, and tubes, and is available in gaskets and in shredded form.¶ It has an extremely high ASTM heat-distortion point of 266 F, will not burn, but can only be molded or fabricated by special techniques. Another disadvantage is that no satisfactory adhesive has been found for the material, although dispersions of the material can be applied and fused in place. The shredded form is useful as pump packing. Polychlorotrifluoroethylene§§ is also chemical- and heat-resistant but is claimed to have somewhat easier processability in molding, etc. Kel-F** polychlorotrifluoroethylene is said to be satisfactory as a bearing material. Molded or machined parts are useful for pump diaphragms and valve seats. Ingenious plug valves in

highly corrosion-resistant Durimet 20 alloy and Chlorimet 3 alloy employ Teflon polytetrafluoroethylene as a sleeve and washerlike diaphragm.†† Dispersions of the material are available for application by spraying, dipping, or brushing to be subsequently fused in place at temperatures of 437–650 F applied for a period of 2 to 5 minutes.

Polyamide plastics such as nylon‡‡ are valuable in the form of gears, cams, bearings, idler rollers, pressure plates, and friction tracks in cameras, projectors, printers, and processing machines. They have the advantage that no lubrication is required. Nylon bearings, however, may break down at excessive speeds. Nylon is fairly rapidly attacked by mineral acids but mild organic acids and strong alkalis have a negligible effect.¶¶ The chemical industry has shown an increasing tendency to replace metals by plastics.¶¶¶ This tendency is dependent upon the ability of the particular plastics to resist chemical attack, and has been intensified by the difficulties in obtaining certain metals.

Synthetic Thermosetting Resins and Plastics

In the manufacture of thermosetting plastics, heat is employed to mold and set the resin to an irreversible form. Molded materials of the thermosetting variety are, therefore, not subject to further forming, molding, or distortion by the action of heat. A large class of this type of materials is represented by the phenol-formaldehyde condensation products. Although these are generally resistant to the dilute acids and fixing solutions used in photography and to low and moderately alkaline developers at normal temperatures (68 F, 20 C), they are, however, not usually resistant to strongly alkaline (caustic) developers, strong oxidizing solutions, or to rapid processing developers at elevated temperatures. Containers may be molded§§§ in intricate patterns which

†† Durco Type F Plug Valve, The Duriron Co., Dayton 1, Ohio.

‡‡ By E. I. du Pont de Nemours & Co., Inc., Polychemicals Department, Wilmington 98, Del.

§§ By Bakelite Division, Union Carbide & Carbon Corp., 30 East 42nd Street, New York 17, N. Y.

¶¶ Catalin Corp., New York 16, N. Y.

¶¶¶ Durez Plastics and Chemicals, Inc., North Tonawanda, N. Y.

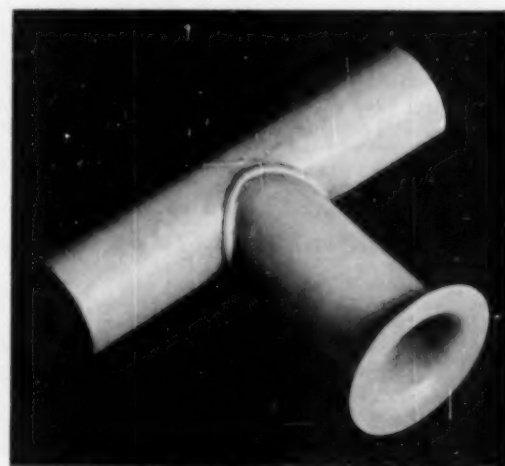


Fig. 4. Hot-Air Jet-Welded and Heat-Flanged Pipe "T" of Non-plasticized Rigid Polyvinylchloride.

* Model L Flame Spray Powder Pistol, Schori Process (Division of Ferro-Co Corporation), 8-11 Forty-third Rd., Long Island City 1, N. Y.

† E. I. du Pont de Nemours & Co., Inc., Plastics Dept., Arlington, N. J.

‡ "Hot Jet" Air Heater or air torch (electrically heated), DeBell & Richardson, Inc., Hazardville, Conn.

§ For example, Boltaron 6200 Series (based on Geon 404 resin), in sheet, rod, tube, and standard threaded pipe and fittings; marketed by H. N. Hartwell & Son, Inc., Boston, Mass.

Geon 404 resin, comminuted form only, B. F. Goodrich Chemical Co., Rose Bldg., Cleveland 15, Ohio.

¶ Tygon resin (specify properties required), The United States Stoneware Co., Akron 9, Ohio.

|| E. I. du Pont de Nemours & Co., Inc., Polychemicals Dept., Wilmington 98, Del.

¶ United States Gasket Co., P. O. Box 93, Camden, N. J.; see reference 49, pp. 1662-63.

** M. W. Kellogg Co., Jersey City, N. J.

hold their shape even in hot water. Laminated-fabric-reinforced and graphite-containing phenolic condensation products* may be used for certain bearings and other small parts. Representative material is available in sheet, rod, and pipe stock and has been used with success for processing machine parts.

I. Organic Coatings and Linings

Organic coatings may consist of (1) relatively thin coatings of lacquer or corrosion-resisting paints applied by brushing, dipping, or spraying, or (2) thicker organic coatings, which, in certain instances, result from the application of viscous, almost gel-like solutions to the surfaces of processing tanks, sometimes with the aid of an inert woven or fine-mesh screen lining. Where the thermoplastic resins can withstand heat sufficiently they may be used in powder form to be melted and flame-sprayed by means of a special flame pistol or pressure torch onto metal surfaces which have previously been sand- or alumina-blasted. Plastisols, or mixtures of some synthetic resins and plasticizers in colloid dispersion form may be coated on surfaces and then fused in place as a continuous film by a blowtorch or similar source of heat.

For continuous service in contact with solutions, coatings applied as lacquers and paints are usually undesirable, since the materials as a general rule are not sufficiently impervious to moisture and acid vapors to prevent attack of the base metal.

Tank linings applied in sheet form with suitable cements and with the edges heat-welded or vulcanized together often prove satisfactory. Custom lining work is the specialty of a number of firms in the chemical engineering and corrosion protection fields.

J. Wood, Paraffined Wood, and Resin-Bonded Plywood

Wood has been used for developing, fixing, and washing purposes because of its relatively low cost, ease of working, availability, and fair resistance to attack by the usual processing solutions. Now, in view of its increasing cost, variable quality, and other objectionable features, it may not be the cheapest material in the long run for use in tank construction, or even for racks and reels. For model construction and pilot process construction, it is still used, although plastics, paraffined wood, and waterproof resin-bonded plywood are making inroads in this field.

The most satisfactory varieties of wood for the construction of tanks are cypress, spruce, redwood, maple, and teak. With developers, old wooden tanks tend to stain a fresh solution. With fixing baths, as in storage tanks, the crystallizing hypo causes splitting of the wood. This may be minimized by keeping the level near the top. For use as fixing-bath containers or for temperature-controlling water jackets, paraffined wood is preferable.

Wooden tanks frequently accumulate fungus growths on the inside and outside, and this accumulation requires regular cleaning. Formation of slime is not peculiar to wooden tanks, but the action of the fungus may be more destructive to wood. The porous surface is less easy to clean effectively unless it is kept well lacquered. The

growth of fungi can be minimized by occasionally filling the tank with an approximately 0.1% solution of sodium hypochlorite (Clorox, "101," Sunny Sol, etc., diluted 1:30), allowing it to stand several hours or overnight, and then thoroughly rinsing the tank. Rooms should be thoroughly ventilated to avoid attack of metal equipment and instruments by the small concentration of chlorine in the air. Another method is to employ a solution of Dowicide G† fungicide (sodium pentachlorophenate) at a strength of 1 part in 1000 parts of water. This solution has the advantage that no volatile substance is present and it will not corrode metals. In preparing the solution, care should however be taken to avoid inhaling the dry powdered material, as it is toxic.

Paraffin-impregnated wood is generally more satisfactory than unwaxed wood for the construction of tanks and water jackets. It is not porous and does not tend to accumulate fungus slime, since it is more easily kept clean. It has the disadvantage of being too heavy for sizable equipment intended for manual handling. It is brittle and breaks easily if dropped. Methods of impregnating various kinds of wood with paraffin were investigated by Eberlin and Burgess,¹⁰¹ who recommended soaking cypress or spruce wood for twelve hours, followed by immersion in molten paraffin wax for two hours at 250 F (120 C). The treated wood when removed from the paraffin bath is wiped with a cloth to remove the excess wax. Water tight joints in paraffined wood are best made by grooving the pieces of wood to be joined together, as for a T-joint, and inserting tightly in the groove a small piece of unparaffined wood. When placed in water, the untreated strip swells and completely caulks the seam.¹⁰² Rectangular tanks should be held together with brass or monel alloy tie-bolts. Corrosion-resisting wood screws may be used in minor sections, but they should be of sufficient length to insure holding.

Among wood products, thermosetting phenolic resin-bonded plywood has been used with considerable success for intermediate-sized and small-scale tanks, trays, and troughs for use with the usual processing solutions. Such tanks should be carefully joined, and the surface, both inside and out, treated with a suitable protective paint or lacquer to decrease water absorption. Where moisture absorption, as from solutions, is involved, hot-press thermosetting phenolic resin-bonded plywood should be used.^{103, 104} Casein adhesive is not satisfactory, and cold, relatively low-temperature setting resins, such as urea-formaldehyde, are not particularly satisfactory.

For a review of developments in wood, laminated and plywood, and modified wood products, extensive summaries¹⁰⁵ are available. Recent advances in wood-preservation treatments applicable to support timbers and other structures not immersed in the solutions are also discussed in the references cited.

SUGGESTIONS ON FABRICATION AND MAINTENANCE

Before the design of processing equipment and installations can be chosen and the details worked out, the type and general characteristics of the constructional materials

† Dow Chemical Co., Midland, Mich.

* Synthane resin, Synthane Corp., Oaks, Pa.
Phenolite Laminated Plastic, National Vulcanized Fiber Co., Wilmington, Del.

should be known. Where metal tanks and equipment are to contain photographic solutions or are to be immersed in them, it is important to (1) choose a single metal or alloy in preference to more than one for a given solution, and (2) consider fabrication by welding in preference to either soldering or silver-solder brazing with dissimilar metals or attaching with bolts or screws. If, however, bolts or screws are required in stainless-steel or other stainless-alloy equipment, they should be of the same general type of metal or alloy, or possibly of Inconel, if the corrosion requirements are not too stringent. Monel or nickel bolts darken in the air but may be satisfactory if the apparatus is not subjected to immersion during fixing or strong oxidizing agent solutions. The usual nickel-plated steel screw products are frequently not satisfactory, because the plating is seldom impermeable to the solutions.

Materials may be selected as given in Tables IV-VII or qualitatively tested for corrosion and chemical resistance as well as for photographic inertness by means of convenient accelerated tests, as described in the section "Corrosion and Photographic Tests of Sample Materials" (see page 82). If a large-scale installation is contemplated, confirmatory tests should be made of the metal or non-metal material selected before the equipment is constructed.

A useful procedure with a field kit for rapid identification of some nickel alloys and stainless steels by means of chemical spot tests was presented in 1949.¹⁰⁸ A portion of these tests dealing with the differentiation between molybdenum-free and molybdenum-containing stainless steels is given in a subsequent section of this paper. A kit of this type is illustrated in Figure 5.

When choosing a material, a liberal allowance in material cost must be made if relative permanence and trouble-free continuous operation are desired. When confronted by a choice between less or more resistant types of material, for example, moderately resistant stainless steel Type 304 and the highly resistant Type 316, the more resistant variety should be selected.

A sulfur-free synthetic elastomer, such as neoprene, should preferably be used in place of natural rubber for resilient or flexible parts. For conducting tubes and pipes, several types of plastics are available as well as the stainless alloys. Rubbing or bearing contact between tough alloys, such as stainless steels, is usually

undesirable, because undue friction with "seizing" or "galling" of the metal surface can result. In cases of repeated rubbing contact, an extremely hard alloy, such as Stellite No. 1* alloy rubbing on the same material is suitable for long service. When stainless steel is used, for example as a shaft, one of the nylon plastics may be chosen as a bearing, provided mineral acids are not present and velocities are not excessive.

Processing temperatures of about 68 F (20 C) have heretofore been considered usual but recent developments in so-called rapid or ultrarapid processing usually require substantially higher temperatures to values of the order of 125 F to 150 F. Thus, the designer of the equipment should take into account the fact that the temperature may be changed considerably. Thermoplastic materials are subject to rapid distortion near their characteristic heat-distortion points and some cold flow even below this temperature.

Most of the highly corrosion-resistant stainless steels are austenitic alloys which are non-magnetic in their passive condition. However, for apparatus, valves, etc., requiring magnetic attraction to move a given part, certain fairly corrosion-resistant stainless-steel materials have recently been produced.

Tanks with plastic, resin, or rubberlike organic linings^{107, 108, 109} to resist attack of especially corrosive solutions, such as bleaches and certain toning solutions, should be designed with round corners of at least 1/8- to 1/4-inch radius on all exposed edges and outside corners. Fillet welding should also be used on all outside corners and recesses. This practice will prolong the life of the linings manifold. Stainless-alloy equipment and tanks should be designed and located to permit easy cleaning and to avoid crevices where stagnant localized corrosion may gain a foothold, with eventual pitting and perforation of the material.

Passivation-Pickling Treatment of Stainless Steel

It is now recognized that the so-called passivation treatment of stainless steel in warm nitric acid of 20 to 30% is (1) chiefly useful in removing ordinary iron, iron compounds and impurities, such as inclusions from the surface of the alloy, to enable it to present a clean uniform equipotential surface, and (2) to supply a sufficient oxidizing state to the surface of the alloy which may involve adsorption of nitrate,^{110, 114} nitric oxide, or the complete absence of interstitial or adsorbed hydrogen. Passivation of stainless steels has been accomplished in hot sulfuric acid solution instead of nitric acid.^{111, 112, 113} In this case, it appears that primarily the cleaning, and secondarily the atmospheric oxygen is responsible for the passivation, since an active state which permits corrosion is produced when the process occurs in a vacuum. Potential measurements thereafter show a slow but steady increase to an equilibrium condition in air.^{111, 112} Uhlig and Wallace¹¹⁵ showed experimentally that even hydrochloric acid solution (3-12.5 normal), provided it contains a sufficiently active corrosion-inhibitor, can impart a fairly passive state to an 18-8 stainless-steel surface but this is not quite as good as 30% nitric acid alone. Hydrochloric acid without the inhibitor checks passivation and produces an active state in stainless steels.

* Haynes Stellite Co., Kokomo, Ind.



Fig. 5. Test Kit for Rapid Identification of Some Nickel Alloys and Stainless Steels.

Steel manufacturers often use a combination of nitric and hydrofluoric acid to passivate and pickle stainless steel, probably because of silicious impurities. However, the following nitric acid treatment has been found to give favorable results for normal use:

Solution: Nitric acid, concentrated 4 parts
Water 10 parts

Temperature: 120-140 F.

Time: 1/2 hour, followed by thorough washing to remove the acid.

Precautions: Wear rubber gloves, protective clothing, safety goggles, gas mask for acid fumes; treat in a fan-ventilated chemical "hood" or outdoors.

Stainless-steel samples for corrosion tests should be passivated if presence of impurities of iron is suspected from cutting or fabricating. The treatment is also desirable for stainless-steel fabricated parts after welding, forming, bending, filing, grinding, or machining.

Notes on Welding of Stainless-Steel Tanks*

Stainless steel used for construction of photographic processing tanks should be of the low-carbon grades—AISI Types 304, 316, and 347 with 0.08% maximum carbon. Low-carbon content is necessary in order to inhibit the formation of chromium carbides in the weld area. Excess carbides lead to intergranular corrosion.

For tanks which are large enough to hold 50 gallons or more, stainless-steel sheets of at least 16-gauge thickness should be used. Where possible, corner welds should be avoided, particularly if the sheets on the inside of the tank are to be polished. In other words, the bottoms and sides should be so formed that the joints will come one inch or more from the corners so that the seams will be easier to grind and a straight butt type of seam can be welded. Stainless-steel sheets should be fully annealed and, so the tanks may be cleaned easily, they should have at least a No. 2-B finish.

Many of the commonly accepted methods of welding ferrous materials have not been found to give satisfactory results when welding the non-stabilized types of stainless steels. The oxyacetylene, carbon-arc, and the atomic-hydrogen processes do not give good results either because of the wide heat line obtained or because a poor-quality weld may result. The preferred method is the metallic-arc, although one of the newer techniques, the inert-gas (Heliarc) process may be used, but technique must be carefully controlled to avoid possible overheating of the metal from the gas envelope.

It has been found when welding the unstabilized AISI Types 304 and 316 by the preferred methods indicated that water-cooling during the welding process is effective in preventing the formation of chromium carbides in the weld area. The water-cooling is done by directing a stream of water at the back side of the sheet just behind the welding arc. Weld rod and water stream should follow along together on opposite sides of the sheet. With the stabilized material, AISI Type 347, such water-cooling is not necessary, since the columbium in this steel prevents the formation of harmful chromium carbides. The relatively new extra-low-carbon grades (AISI Types

304L and 316L)† with 0.03% maximum carbon are also comparatively free from carbide precipitation and do not require water-cooling during welding, provided an experienced welder does the work. However, these stabilized and extra-low-carbon grades are somewhat more costly than the regular types.

Such items as joint preparation, amperages, voltages, weld-rod sizes and fixturing should correspond to accepted industrial standards, and those prescribed by the electrode manufacturers are generally acceptable. The electrodes chosen should give a weld deposit of the same analysis as the base sheets. Lime-coated rods and d-c current are preferred. Welding techniques and the design of tanks and joints should be such as to avoid crevices which might give rise to serious localized corrosion. All welding flux and weld scale should be removed by chipping, grinding, or wire brushing. Only brushes with wires of corrosion-resistant materials, such as stainless steel, K-Monel, or Z-Nickel, should be used, as ordinary steel brushes lead to rusting and discoloration.

As a final operation it has been found desirable that tanks be passivated to clean the surface of iron or other metal contamination that might have become imbedded in the surface of the stainless-steel sheets during fabrication. Passivation may be accomplished by immersing the tank in a 20% solution of nitric acid by weight at 120-140 F for 1/2 hour, followed by thorough rinsing in clean water. This is essentially the treatment recommended above.

Cleaning, Care, and Corrosion Peculiarities of Stainless-Alloy Equipment

The life of tanks, trays, and other equipment made of the passive stainless alloys, such as the 18-8 stainless steels, Inconel, and even Type 316 or 317 molybdenum-containing stainless steel will be increased greatly if the surfaces are cleaned regularly and properly to remove any occasional spots or deposits of iron or other impurities. If such impurities are left alone, the alloy may lose its passive nature in this area and corrode faster, causing pits in some alloys.

For mild cleaning of spots and deposits from the surface, it is good practice to employ fine pumice, finely bolted whiting, or alkaline household cleansers containing similar material, rubbing, if possible, in the direction of the original surface grinding. If brushes are used, they should be of fiber. Steel wool should *never* be used. If the surface has become highly contaminated with iron rust, this can be removed with a 5-10% solution of warm citric acid or sodium citrate, followed by thorough washing. In cleaning, attention should be given to areas at joints, welds, or surface where impurities might collect or corrosion develop.

Stainless alloys, such as the austenitic stainless steels and Inconel, depend for their corrosion protection partly on the nature of the various components as alloyed,

† Note that the molybdenum content of the extra low carbon grade Type 316L is given as 1.75-2.5%. For use with acid stop baths or acid fixing baths in closed tanks or systems and with rapid fixing baths containing appreciable concentration of chloride in either open or closed vessels or systems, a molybdenum content preferably near the upper limit of this range and not lower than 2.0% should be specified. This does not alter the range of molybdenum 2.5-3.0% suggested here (see Part II of this paper) to be specified for the Type 316, which contains molybdenum 2.0-3.0% and carbon 0.10% maximum.

* The authors are indebted to H. H. Brown, Metallurgical Laboratory, E. C. and M. Division, Eastman Kodak Company, Rochester, N. Y., for the preparation of this section.

Table IV

SUMMARY OF MATERIALS AND SUGGESTIONS FOR THEIR USE
METAL MATERIALS ROLLED, DRAWN, OR WROUGHT

	Chemical and Photographic Suitability										Equipment Suitability							Remarks
	1D	2D	AR	1F	2F	3F	BB	BF	W	Ha	Ft	Pi	Ra	Pu	Sm	Ta		
<i>Metals, Rolled, Drawn, or Wrought</i>																		
Aluminum	N	N	N	N	N	N	N	N	N	N	R	R	N	N	N	R	Distilled water; for structural supports by a few users.	
Brass, red (copper 85% min.)	N	N	N	N	N	N	N	r	N	N	R	R	N	N	R	r	Tanks and piping principally; avoid excessive flow velocities in pipes or attrition due to undissolved solids; trays excluded.	
Bronze, silicon	N	N	N	N	N	N	N	r	N	N	R	R	N	N	R	r	Tanks and piping principally; avoid excessive flow velocities in pipes or attrition due to undissolved solids; trays excluded.	
Carpenter 20 alloy	R	R	R	R	r	R	R	N*	R	N	R	R	R	R	R	R	See Brass, red.	
Copper	N	N	N	N	N	N	N	r	N	N	R	R	N	N	R	r		
Hastelloy C alloy	R	R	R	R	R	R	R	R	R	N	R	R	R	R	R	N	Inconel X alloy: hardened springs. Use only with closed, filled piping for developers of moderate alkalinity.	
Illum G alloy	R	R	R	R	R	R	R	N*	R	N	N	N	R	R	R	N		
Inconel alloy	R	R	r	r	N	N	r	r	R	R	R	R	R	N	R	R		
Iron	r	N	N	N	N	N	N	N	N	N	R	R	N	R	N	N	Sink and small-tank linings; weights for clips.	
Lead	R	N	N	N	N	N	r	R	N	N	r	r	N	N	R	N		
Monel alloy	r	r	N	N	N	N	N	N	R	N	R	R	R	R	R	R	Distilled water stills and piping.	
Nichrome alloys, various	r	r	N	N	N	N	N	N	N	N	N	N	N	N	N	N		
Nickel	R	R	N	N	N	N	N	N	r	N	R	R	R	R	R	R		
Nickel silver	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N		
Silver	R	R	R	N	N	N	N	N	R	N	N	N	N	N	R	N		
Silver solder (silver 45% min.)	r	r	r	N	N	N	N	N	r	N	N	N	N	N	N	N		
Solders (tin-lead, various %)	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N		
<i>Stainless steels</i>																		
AISI Type 302	R	R	r	r	N	N	N	N*	r	R	R	R	R	N	R	R	Hardened springs; wearing parts, sprockets, chain, etc.	
AISI Type 303 (without selenium)	R	R	r	r	N	N	N	N*	r	R	N	N	R	N	R	N		
AISI Type 303 (selenium-bearing)	R	R	N	N	N	N	N	N	r	R	N	N	R	N	R	N		
AISI Type 304	R	R	r	r	N	N	N	N*	r	R	R	R	R	N	R	R		
AISI Type 304L (extra-low-carbon)	R	R	r	r	N	N	N	N*	r	R	R	R	R	N	R	R		
AISI Type TS316 (specify molybdenum, preferably near 2.5% and not lower than 2.0%)	R	R	R	R	r	r	R	N*	R	N	R	R	R	N	R	R		
AISI Type 316	R	R	R	R	R	R	R	N*	R	N	R	R	R	N	R	R		
AISI Type 316L (extra-low-carbon) (specify molybdenum, preferably near 2.5% and not lower than 2.0%)	R	R	R	R	r	r	R	N*	R	N	R	R	R	N	R	R		
AISI Type 321	R	R	r	r	N	N	N	N*	r	R	R	R	R	N	R	R		
AISI Type 347	R	R	r	r	N	N	N	N*	r	R	R	R	R	N	R	R		
AISI Type 420	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N		{ Hardened springs; wearing parts, sprockets, chain, etc.
AISI Type 430	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N		
Tantalum	R	N	R	R	R	R	R	R	R	N	R	R	N	N	R	N		Fabrication procedures not well established.
Titanium (tentative)	R	R	r	r	r	r	r	R	R	N	N	N	N	N	N	N		
Tin	N	N	N	N	N	N	N	N	N	N	R	R	N	N	N	N	Distilled-water piping.	
Zinc	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N	Galvanized tap-water piping.	

* Substitute "r" for "N," indicating short-duration or intermittent use only with ferricyanide-containing bleaches as supplied under trade names for various color processes.

partly on the maintenance of a clean equipotential surface, and finally on their property of requiring an invisible and ordinarily self-healing nitrate, oxide, or oxygen film which imparts a passive state to the alloy. This passivating film or state is usually present but can become disturbed or impaired. The metal will then become active and corrode by being subjected to more than temporary contact with certain metals. These metals are notably iron and its compounds; certain chemicals or their solutions, including appreciable concentrations of halogen salts, such as chlorides, bromides, iodides, and

also thiocyanates, particularly in neutral or acid solutions, and the corresponding halogen elements and acids, hydrochloric, etc.; sulfuric acid more than 5%; contact with ordinary iron and steel; iron impurities (as from pipes) or iron (ferric or ferrous) compounds, including ferricyanides; mercury salts, including mercuric chloride; and sulfurous acid (water containing sulfur dioxide) condensed vapor, as in a closed space over acid fixing baths. An exception to the latter is a molybdenum-containing stainless steel, such as Type 316. Possible detrimental action of the compounds mentioned is also

Table V

SUMMARY OF MATERIALS AND SUGGESTIONS FOR THEIR USE
CAST METAL MATERIALS

	Chemical and Photographic Suitability									Equipment Suitability							Remarks
	1D	2D	AR	1F	2F	3F	BB	BF	W	Ha	Ft	Pi	Ra	Pu	Sm	Ta	
Metals, Cast																	
Bronze, silicon, e.g., Everdur alloy	N	N	N	N	N	N	N	r	N	N	R	N	N	N	R	N	Trays excluded
Chlorimet 3 alloy	R	R	R	R	R	R	R	N*	R	N	R	R	R	R	R	N	"Sm" = small parts only
Durichlor alloy	N	N	N	N	N	N	N	N	N	N	R	R	N	N	N	N	Chemical drain piping
Durimet 20 alloy	R	R	R	R	R	R	R	N*	R	N	R	R	R	R	R	N	"Sm" = small parts only
Duriron alloy	N	N	N	N	N	N	N	N	N	N	R	R	N	N	N	N	Chemical drain piping
Hastelloy C alloy	R	R	R	R	R	R	R	R	R	N	R	R	R	R	R	N	"Sm" = small parts only
Illum G alloy	R	R	R	R	R	R	R	N*	R	N	R	R	R	R	R	N	"Sm" = small parts only
Inconel alloy	R	R	r	r	N	N	r	r	R		R			R	R		"Sm" = small parts only
Ni-Resist alloy	N	N	N	N	N	N	N	N	N	N	R	R	N	N	N	N	Chemical drain piping
Stainless steels																	
ACI Designation, CF-7	R	R	r	r	N	N	N	N*	r	N	R	N	N	N	R	N	"Sm" = small parts only
ACI Designation, CF-7C	R	R	r	r	N	N	N	N*	r	N	R	N	N	N	R	N	"Sm" = small parts only
ACI Designation, CF-7M	R	R	R	R	R	R	R	N*	R	N	R	N	N	R	R	N	"Sm" = small parts only
ACI Designation, CF-7MC	R	R	R	R	R	R	R	N*	R	N	R	N	N	R	R	N	"Sm" = small parts only
Stellite No. 1 alloy	R	R	R	R	R	R	R	R	R	N	N	N	N	N	R	N	"Sm" = Small parts for hardened wear surfaces
Worthite alloy	R	R	R	R	R	R	R	N*	R	N	R	N	N	R	N	N	

* Substitute "r" for "N," indicating short-duration or intermittent use only with ferricyanide-containing bleaches as supplied under trade names for various color processes.

Table VI

SUMMARY OF MATERIALS AND SUGGESTIONS FOR THEIR USE
COATED METALS AND CLAD METALS

	Chemical and Photographic Suitability									Equipment Suitability							Remarks
	1D	2D	AR	1F	2F	3F	BB	BF	W	Ha	Ft	Pi	Ra	Pu	Sm	Ta	
Coated Metals																	
Glass-coated steel	R	R	R	R	R	R	R	R	R	N	r	r	N	r	r	r	Usually trays and small tanks only because of possibility of cracking and difficulties in re-pairing.
Hard rubber-coated steel	R	R	R	R	R	R	R	R	R	N	R	R	N	R	R	R	
Polyethylene or Polythene resin-coated metals	R	R	R	R	R	R	R	R	R	N	R	R	N	r	R	R	
Saran polyvinylidene resin-coated steel	R	R	R	R	R	R	R	R	R	N	R	R	N	R	R	R	
Vitreous-enameled steel	R	R	R	R	R	R	R	R	R	N	N	N	N	N	R	r	Usually trays and small tanks only.

Clad or Laminated Metals: Many stainless steels, and Inconel alloy, are available laminated to ordinary steels. Although somewhat lower in cost, these laminates are usually not recommended, since skillful and exacting welding techniques are required, and the outside surfaces of vessels must be adequately protected against corrosion by coatings.

generally less with Type 316, although the difference is one of degree, and long contact of most of the materials with even this alloy should be avoided.

When any of the detrimental compounds have been in contact with the stainless alloys, they should be washed away thoroughly with water; the vessels should be refilled with other solution, or water, or drained and dried so as to prevent the drying of residual salts on the surface.

Rapid Spot Tests for Identifying Some Metals, Nickel Alloys, and Stainless Steels

In a paper presented in 1949 and subsequently published, a field kit and procedures were described for rapid spot tests of some nickel alloys and stainless steels. A kit similar to that described is shown in Figure 5. Among the tests proposed was a method for differentiat-

ing between molybdenum-containing stainless steel, for example, Type 316, and molybdenum-free stainless steel, such as Type 304. The method is essentially that previously published except for slight changes to adapt the test to porcelain spot-plate testing instead of the use of white (photographic) blotting paper. More recently a new pamphlet has appeared¹¹⁶ which contains a variety of methods outlining simple analysis and other procedures for the rapid identification (spot testing) of 100 different metals and alloys, some bearing trade names.

The following method, cited above, is satisfactory for differentiating between Type 316 or other molybdenum-containing stainless steel and Type 304 or other stainless steel which does not contain an appreciable amount of molybdenum. It is assumed that the samples to be tested are austenitic and therefore non-magnetic as tested with a magnet.

Table VII

SUMMARY OF MATERIALS AND SUGGESTIONS FOR THEIR USE
NON-METAL MATERIALS

	Chemical and Photographic Suitability									Equipment Suitability							Remarks
	1D	2D	AR	1F	2F	3F	BB	BF	W	Ha	Ft	Pi	Ra	Pu	Sm	Ta	
<i>Plastics and resins, thermoplastic</i>																	
Acrylate resins	R	R	R	R	R	R	R	R	R	..	r	r	r	N	r	N	Somewhat brittle.
Lucite resin, various	R	R	R	R	R	R	R	R	R	..	r	r	r	N	r	N	Somewhat brittle.
Plexiglas resin, various	R	R	R	R	R	R	R	R	R	..	r	r	r	N	r	N	Somewhat brittle.
Cellulose acetate-butyrate																	
Tenite II brand	R	N	R	R	R	R	R	R	R	..	R	R	R	N	R	N	Pipes require frequent support.
Nylon, various types in plain and graphited	R	R	r	R	R	R	N	R	R	..	N	N	N	N	N	N	Bearings for relatively light loads and low velocities; gears.
Polyethylene	R	R	R	R	R	R	R	R	R	N	r	r	N	N	N	N	Tank linings flame-sprayed on steel; piping for low pressure only; sheeting for floating covers.
Polythene materials	R	R	R	R	R	R	R	R	R	N	r	r	N	N	N	N	
Polytetrafluoroethylene (Teflon brand)	R	R	R	R	R	R	R	R	R	N	N	N	N	N	N	N	Gaskets, pump and valve packing and seals.
Polymonochloroethylene (Kel-F brand)	R	R	R	R	R	R	R	R	R	N	N	N	N	N	N	N	Gaskets, pump and valve packing and seals.
Polystyrene, various	R	R	R	R	R	R	R	R	R	..	r	r	R	N	R	N	Some grades are brittle; avoid elevated temperatures.
Polyvinylchloride, rigid (Geon 404 resin molded as Boltaron 6200 Series, other molded products such as Agilide, Amcoflex, and Lucoflex)	R	R	R	R	R	R	R	R	R	..	R	R	R	N	R	N	Heat-distortion point, 170 F.
Polyvinylidene materials, (Saran brand)	R	R	R	R	R	R	R	R	R	..	r	r	R	N	R	N	Loss of plasticizer with leaching in time may cause embrittlement.
<i>Synthetic rubber and styrene copolymers</i>																	
(Royalite brand)	R	R	R	R	R	R	R	R	R	N	N	N	N	N	r	N	Available as sheet.
(Uscolite brand)	R	R	R	R	R	R	R	R	R	N	R	R	N	N	N	N	Available as pipe and fittings.
(RIJI-TUF brand)	R	R	R	R	R	R	R	R	R	N	R	R	N	N	r	N	Heat distortion point, 125-130 F.
<i>Plastics and resins, Thermosetting</i>																	
Hard rubber	R	R	R	R	R	R	R	R	R	N	r	r	R	R	R	N	Somewhat brittle
Phenol-formaldehyde	R	N	R	R	R	R	r	r	R	r	N	N	r	N	Somewhat brittle unless re-inforced.
Phenol-formaldehyde (canvas reinforced)	R	N	R	R	R	R	r	r	R	r	R	r	R	N	For loose submerged bearings; material swells in solutions; gears.
(graphited)	R	N	R	R	R	R	r	r	R	For bearings.
Polyester with Fiberglas reinforcement	R	N	R	R	R	R	r	R	R	..	r	r	r	N	R	N	Pipe and fittings only.
(Glasweld brand)	R	N	R	R	R	R	r	R	R	N	r	r	N	N	N	N	
<i>Rubber and Synthetic Elastomers</i>																	
Natural rubber	R	R	R	R	R	R	R	R	R	N	N	R	N	N	N	N	Tubing.
Neoprene, various types	R	R	R	R	R	R	R	R	R	N	N	R	N	R	R	N	Tubing, gaskets.
Polyvinylchloride, flexible (Korozeal brand, flexible; Tygon brand, flexible)	R	R	R	R	R	R	R	R	R	N	N	R	N	N	N	N	Hot water or warm solutions cause loss of plasticizer and flexibility.
<i>Miscellaneous</i>																	
Alberene stone, specify Grade 25	R	R	R	R	R	R	R	R	R	r	Grade 25 meets Bureau of Standards specifications for photographic purposes; sinks and tanks.
Carbon	R	R	R	R	R	R	R	R	R	N	r	r	N	N	r	N	Brittle.
Carbon-plastic composition (Carbate brand)	R	N	R	R	R	R	R	R	R	N	r	r	N	N	N	N	
Glass, Heat-resisting (Pyrex brand)	R	R	R	R	R	R	R	R	R	N	r	r	N	r	r	N	Special pipe fittings and couplings required.
Vitreous stoneware (chemical stoneware)	R	R	R	R	R	R	R	R	R	N	N	N	N	N	r	r	Tanks and storage vessels
Wood (for example, cypress)	r	r	R	r	r	r	N	R	R	N	N	N	N	N	r	r	Tanks and storage vessels.
Wood (paraffin-impregnated)	R	R	R	R	R	R	R	R	R	N	N	N	N	N	r	N	Tanks and storage vessels.
Plywood (fully waterproof phenolic resin-bonded)	r	r	R	r	r	r	N	R	R	N	N	N	N	N	r	N	Trays and small tanks for intermittent or short-duration runs.

The following solutions of reagent-grade chemicals are used in the test:

- No. 1. Nitric acid, concentrated.
- No. 4. Hydrochloric acid, concentrated.
- No. 6. Sodium thiocyanate, 3 grams dissolved in 30 milliliters of distilled water.
- No. 7. Stannous chloride, crystal ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) 6.5 grams dissolved in 5 milliliters of concentrated hydrochloric acid, using heat to obtain solution. This solution is then diluted with 25 milliliters of distilled water.

The test is performed as follows:

1. Place 1 drop of solution No. 1 and 1 drop of solution No. 4 on a clean spot on the specimen to be tested, and allow them to react for 30 seconds.
2. Transfer the reaction mixture to a depression of a white spot plate using a medicine dropper.
3. Add 10 drops of distilled water and mix.
4. Add 4 drops of solution No. 6 and mix.
5. Add 6 drops of solution No. 7 and mix.

Results and Conclusions. (a) If the resulting solution is orange-red, the specimen is a molybdenum-containing stainless steel, such as Type 316. (b) If the resulting solution is colorless or pale green, the specimen is a molybdenum-free stainless steel, for example, Type 304.

For other tests to identify nickel, Monel alloy, Inconel alloy, and some stainless steels, reference should be made to the original paper or to the other reference pamphlet cited.

SUMMARY TABLES OF MATERIALS AND SUGGESTIONS FOR THEIR USE

The accompanying lists of kinds and types of materials for the construction of photographic processing apparatus is not complete, but it catalogues some materials considered to be generally satisfactory for the purposes indicated. Omission of a material or type of material does not imply that such a product is unsatisfactory. For listings of metal and alloy materials that are generally unsatisfactory in given solutions, see page 87.

Tables IV, V, VI, and VII list materials whether they do or do not appear to give favorable results, according to the type of service indicated. Continuous service is implied unless otherwise stated.

In using the tables reference should first be made to the section headed: *Chemical and Photographic Suitability*, and second to the section: *Equipment Suitability*. Thus, the equipment suitability, as here considered, is only applicable where the chemical and photographic suitability is indicated by either "R" or "r". *Equipment Suitability* is based upon a consideration of physical properties, availability of a material in certain forms, practical fabrication difficulties, and other points affecting the advisability of utilizing the material for a given type of equipment: for example, the tendency to plate out silver on the metal in the case of film hangers, ease of breakage, and difficulty of repair.

Key:

- R = Results favorable
- r = May be used with reservations
- N = Not desirable
- 1D = Moderate-alkalinity developer
- 2D = Caustic developer
- AR = Mild acid rinse or stop bath

- 1F = Aluminum hardening fixing bath
- 2F = Aluminum hardening rapid fixing bath
- 3F = Chromium hardening fixing bath, or chromium hardening stop bath.
- BB = Bleach, bichromate, for black-and-white reversal processing (containing potassium bichromate and sulfuric acid).
- BF = Bleach, ferricyanide (containing potassium ferricyanide and potassium bromide)
- W = Washing

Note: Rolled, drawn, or wrought stainless steels are designated by the type number as specified by the American Iron and Steel Institute (AISI).

Cast stainless steels are given by the respective designations as specified by the Alloy Casting Institute (ACI).

Ha = Film hangers; also devices of a type that do not remain continuously in a given solution, and can easily be cleaned; tanks and trays for short-duration use.

Ft = Fittings, particularly pipe fittings, valves, and faucets.

Pi = Pipe, including tubing, used for transfer of liquids; usually not frequently cleaned.

Ra = Racks, sprockets (in case of metal only), and idlers which may be continuously or intermittently immersed.

Pu = Pumps.

Sm = Small parts, trays, small tanks, paddles, brackets (in case of metal only); etc., which may remain continuously immersed or in contact with solution.

Ta = Large tanks.

Acknowledgment

The authors desire to acknowledge information supplied by H. F. Betz, H. H. Brown, N. B. Carter, R. M. Corbin, C. E. Ives, H. B. Lea, G. E. Matthews, J. C. Reddig, and R. S. Scott.

References

49. Chemical Engineering Catalogue, 36th edition, Reinhold Publishing Corp., New York 18, N. Y., 1951-52, issued September 1951.
50. See reference 49, pp. 97-100; also Kessler D. W., "The Action of 'Hypo' Solution on Stone Tanks," J. Res. Nat. Bur. Standards, Vol. 16, pp. 161-164 (February 1936).
51. Werking, L. C., "Carbon, Graphite and Karbate as Materials of Construction," Trans. Amer. Inst. Chem. Eng., Vol. 35, pp. 489-503 (1939); see also, Werking, L. C., "Impervious Carbon Equipment," Chem. & Met. Eng., Vol. 46, pp. 362-364 (June 1939).
52. Ford, C. E., "Carbon and Graphite," Ind. Eng. Chem., Vol. 39, pp. 1202-1204 (1947); Vol. 41, pp. 2097-2099 (1949); Gaylord, W. M., *ibid.*, Vol. 43, pp. 2199-2202 (1951).
53. Carbon and Karbate Pipe Installation Manual M-8801A, National Carbon Co., Inc., Dept. C, 30 East 42nd Street, New York 17, N. Y.
54. Rubl, F. F., "Carbon and Graphite Parts," Steel, Vol. 118, pp. 108-110 (May 20, 1946). Products of "Graphitar" (carbon-graphite) described were made by The United States Graphite Co., 1621 Holland Ave., Saginaw, Mich. See also Catalogue G-49 obtainable from this firm.
55. Payne, C. R., Ind. Eng. Chem., Vol. 41, pp. 1781 (1948). Discussion and references to various organic lining and coating materials for concrete tanks.
56. Crabtree, J. I., and Matthews, G. E., "Photographic Chemicals and Solutions," American Photographic Publishing Co., Boston, Mass., pp. 41-45 (1939), out of print but available in libraries.
57. Chem. & Met. Eng., Vol. 40, p. 270 (May, 1933).
58. Herstein, F. E., "Chemical Stoneware," Ind. Eng. Chem., Vol. 39, pp. 1254-1256 (1947).
59. Koenig, J. H., Ind. Eng. Chem., Vol. 40, particularly section on "Chemical Stoneware," p. 1785 (1948); *ibid.*, Vol. 41, pp. 2104-2105, 2107-2108 (1949); with Thomas, R. H., *ibid.*, Vol. 42, pp. 1968-1970 (1950).
60. Smith, R. D., and Corbin, P. E., J. Amer. Ceram. Soc., Vol. 32, pp. 195-198 (No. 6, 1949); see also Koenig, J. H., and Thomas, R. H., Ind. Eng. Chem., Vol. 42, p. 1961 (1950).
61. Blizard, J. R., "Glass," Ind. Eng. Chem., Vol. 39, pp. 1215-1218 (1947).
62. See reference 61, p. 1217.
63. Owens-Corning Fiberglass Corp., Toledo 1, Ohio, Bull. D5.5.2 (Dec. 19, 1945).

64. Whitehurst, B. W., "Miles of Glass Piping Fabricated at Oak Ridge," *Chem. Eng.*, Vol. 53, pp. 112-115 (July 1946).
65. Koenig, J. H., Thomas, R. H., and Shand, E. B., "Glass and Glass Developments for Industry," *Ind. Eng. Chem.*, Vol. 42, pp. 1962-1964 (1950); Koenig, J. H., Snyder, N. H., and Shand, E. B., *Ind. Eng. Chem.*, Vol. 43, pp. 2208-2210 (1951).
66. Koenig, J. H., and Shand, E. B., "Glass for the Chemical Industry," *Ind. Eng. Chem.*, Vol. 41, pp. 2107-2108 (1949).
67. Thies, H. R., and Clifford, A. M., "Plioform—A New Molding Resin," *Ind. Eng. Chem.*, Vol. 26, pp. 123-129 (1934).
68. Fritz, H. T., and Hoover, J. R., "The Chemical Resistance of Rubber as an Engineering Material," Special Technical Publication 13, Symposium on Rubber, Amer. Soc. Testing Materials, Philadelphia, Pa., p. 113 (1932).
69. See reference 56, p. 64.
70. Hoover, J. R., "The Pickling Tank of Tomorrow," *Metals & Alloys*, Vol. 5, pp. 100-102 (May 1934). The Vulcalock method of bonding rubber to steel as developed about 1924 and the 3-ply Triflex joint employing both soft and hard rubber are described and an illustration of the latter is given.
71. Handbook of Hard Rubber and Plastics, American Hard Rubber Co., New York, N. Y., 1951.
72. Crabtree, J. I., "Chemical Fog," *Amer. Ann. Phot.*, Vol. 33, p. 20 (1919).
73. For listing and properties of representative newly developed synthetic elastomers, see "Plastics Handbook for Product Engineers," J. Sasso, McGraw-Hill Book Co., New York, N. Y., pp. 377-443, 1946.
74. "Neoprene Notebook," see Index to Neoprene Notebook Dec. 1951, for page references to subjects in issues 1 through 49, available from E. I. du Pont de Nemours & Co., Inc., Rubber Chemicals Division, Wilmington 98, Del. Subjects include chemical resistance, manufacture of neoprene, and diverse uses.
75. "Neoprene," *Chem. & Met. Eng.*, Vol. 51, pp. 130-133 (January 1944). A brief description of the process of manufacturing neoprene elastomer and flow sheet of the process.
76. Fisher, H. L., "Elastomers," *Ind. Eng. Chem.*, Vol. 39, pp. 1210-1212, particularly p. 1211 (1947).
77. Forman, D. B., and Radcliff, R. R., "State of Cure of Neoprene Vulcanizates," *Ind. Eng. Chem.*, Vol. 38, pp. 1048-1052 (1946).
78. Modern Plastics Encyclopedia and Engineers Handbook, Plastics Catalogue Corp., New York, N. Y.
79. See reference 78, annual editions of 1948 to 1952.
80. See reference 78, 1949 edition, pp. 1134-1152.
81. See reference 78, 1948 edition, pp. 776-779 and accompanying charts (in separate containers).
82. See reference 78, 1950 edition, "Identification of Plastics," pp. 992-1000.
83. See reference 78, 1949 edition, p. 224.
84. Yelton, E. B., "Applications of Plastics in Chemical Equipment," *Chem. Eng. Progress*, Vol. 44, pp. 89-92 (1948).
85. See reference 78, 1950 edition, pp. 305-382.
86. See reference 78, 1950 edition, "Cementing Thermoplastics," pp. 344-350.
87. Brown, S., "How to Turn Plastics," *Popular Mechanics*, Vol. 94, pp. 210-214 (December 1950).
88. Akin, R. B., "Molded Nylon," *Modern Plastics*, Vol. 26, pp. 57-63, particularly pp. 57-58 (June 1949). "Mineral acids attack it (nylon) fairly rapidly, but strong alkalis have a negligible effect;" see also reference 84, pp. 90-91; Cady, E. I., "Nylon as an Engineering Material," *Materials & Methods*, Vol. 26, pp. 80-84 (September 1947).
89. Bossert, R. G., Croft, R. C., and Boord, C. E., "Hydrolysis of Nylon," *J. Chem. Ed.*, Vol. 26, pp. 611-612 (1949). Laboratory analysis methods; also mention of recovery methods using mineral acid hydrolysis of nylon.
90. See reference 78, 1949 edition, pp. 281, 282, and 284.
91. Fox, A. B., and LeLair, G. V., "Redesigned for Plastic Molding," *Modern Plastics*, Vol. 27, pp. 110-111 (September 1949). Redesign of the Kodak Automatic Tray Siphon to employ Tenite II cellulose acetate butyrate, with two mirror image parts finally joined by cementing.
92. "Plastic Pipes Invade New Markets," *Modern Plastics*, Vol. 27, pp. 68-75 (March 1950). Some firms are listed which produce the following kinds of thermoplastic pipe and fittings: Saran, polyethylene, Tenite II, and a new product of polyester glass fiber reinforced material. A discussion of the materials is given. The latter material is relatively untried.
93. "Welding Thermoplastics," see reference 78, 1950 edition, pp. 352-53.
94. Neumann, J. A., "Hot Gas Welding of Plastics," *Modern Plastics*, Vol. 28, pp. 97-102 (November 1950).
95. Jaroff, L. M., "Plastics Can be Joined by Several Welding Methods," *Materials & Methods*, Vol. 33, pp. 74-78 (February 1951). Contains diagram for details on construction of a welding torch for plastics.
96. Kline, G. M., and Seymour, R. B., "Plastics," *Ind. Eng. Chem.*, Vol. 44, p. 2339 (1952).
97. *Modern Industry*, Vol. 20, p. 83 (November 1950). Four firms are known to be producing rigid polyvinyl chloride parts under the respective trade names, Agilide, Ampcollex, Boltaron 6200 Series, and Lucollex.
98. Kline, G. M., "Plastics: Ethylene Polymers," *Ind. Eng. Chem.*, Vol. 41, p. 2133 (1949); *ibid.*, Vol. 42, p. 2002 (1950).
99. Fluorothene, by Union Carbide & Carbon Chemical Corp., K-25 Plant, Oak Ridge, Tenn.; "Fluorothene—A Standard Items Catalogue Listing" (Feb. 24, 1949); referred to by Kline, G. M., "Plastics: Ethylene Polymers," *Ind. Eng. Chem.*, Vol. 41, p. 2133 (1949).
100. Kline, G. M., and Seymour, R. B., "Plastics," *Ind. Eng. Chem.*, Vol. 44, pp. 2339-2343 (1952); see also Kline, G. M., "Plastics," *ibid.*, Vol. 39, pp. 1234-1238; Vol. 40, pp. 1804-1809 (1948); Vol. 41, pp. 1232-1237 (1949); Vol. 42, pp. 2001-2006 (1950).
101. Eberlin, L. W., and Burgess, A. M., "Impregnating Wood with Paraffin," *Ind. Eng. Chem.*, Vol. 19, pp. 87-88 (1927); revised 1928.
102. Crabtree, J. I., Matthews, G. E., and Muchler, L. E., "Materials for the Construction of Photographic Processing Apparatus," *PSA J.*, Vol. 2, pp. 14-21 (December 1936); see particularly p. 17.
103. Stamm, A. J., "Wood: Plywood and Laminated Wood," *Ind. Eng. Chem.*, Vol. 41, p. 2151 (1949).
104. "Technical Plywoods," *Materials & Methods*, Vol. 27, pp. 111-113 (January 1948).
105. Stamm, A. J., "Wood," *Ind. Eng. Chem.*, Vol. 39, pp. 1256-1261 (1947); Vol. 41, pp. 2149-2152 (1949); Vol. 43, pp. 2276-2279 (1951).
106. Lea, H. B., "A Field Test Kit and Procedure for Use in the Rapid Identification of Some Nickel Alloys and Stainless Steels," see ASTM Special Technical Bulletin No. 98, Symposium on Rapid Methods for the Identification of Metals, American Society for Testing Materials, Philadelphia, Pa. (1940), pp. 69-72. Reprints of the particular paper are available from the Society at a standard charge.
107. Tator, K., "Organic Linings for Chemical Equipment," *Corrosion*, Vol. 5, pp. 55-58 (February 1949).
108. McFarland, R., "Combating Corrosion with Rubber Lining," *Corrosion*, Vol. 5, pp. 98-99 (March 1949).
109. Thomas, B., "Nonmetallic Lining for Process Vessels in the Pulp and Paper Industry," *Corrosion*, Vol. 6, pp. 82-88 (March 1950).
110. Paige, H., "Contribution to the Nature of Passivity in Stainless Steels," Massachusetts Institute of Technology Corrosion Laboratory, Technical Report 3, U. S. Office of Naval Research Contract N5ori-78-031-187 (October 1949); see abstract in *Corrosion*, Vol. 7, p. 33 (November 1951).
111. Fontana, M. G., "Surface Studies of Metals from the Corrosion Standpoint," *Corrosion*, Vol. 3, pp. 567-579 (1947).
112. Fontana, M. G., and Beck, F. H., "Nature and Mechanism of Passivity of 18-8S Stainless Steel," *Metal Progress*, Vol. 51, pp. 939-944 (June 1947).
113. Kiefer, G. C., and Renshaw, W. G., "The Behavior of the Chromium Nickel Stainless Steels in Sulfuric Acid," *Corrosion*, Vol. 6, pp. 235-244 (August 1950).
114. Renshaw, W. G., and Ferree, J. A., "Passivating Characteristics of the Stainless Steels," *Corrosion*, Vol. 7, pp. 353-360 (1951).
115. Uhlig, H. H., and Wallace, E. M., "The Effect of Hydrochloric Acid Plus Inhibitor on the Corrosion Resistance of an 18-8 Stainless Steel," *Trans. Electrochem. Soc.*, Vol. 81, pp. 511-520 (1942).
116. "Rapid Identification (Spot Testing) of Some Metals and Alloys," The International Nickel Co., Inc. (Development and Research Division), New York 5, N. Y. (1952), 47 pages. Available upon request to the issuing firm.

THE PRODUCTION OF PHOTOGRAPHIC GELATIN

Joseph H. Cohen*

ABSTRACT

About one-seventh of the 50 million pound U. S. annual production of gelatin is for photography. Raw materials are mainly ossein from beef and water buffalo bones, calfskin hides and splits, and porkskin. Gelatin is extracted by warm water after pretreatment to clean and swell the raw materials. Subsequent drying, grinding, blending, etc. are done with particular attention to sanitation because of bacterial affinity for gelatin. Physical and chemical characteristics are kept constant by laboratory controls and purchases are made on the basis of lot sample. New developments include photographically inert or "basic" gelatins from which natural photographic sensitizers and restrainers have been eliminated during the course of manufacture.

THE DEVELOPMENT of gelatin manufacture in the United States has paralleled the remarkable growth and expansion of the country as a whole. From an industry with a total production worth about \$50,000 annually in 1810, it has developed into one with an annual output worth millions of dollars. As recently as 1933, the United States Department of Commerce reported an annual output of edible gelatin in the United States of 13 million pounds. Today this country consumes almost three times that amount of edible gelatin. Estimates of the quantities of gelatin that will be consumed in the United States this year follow:

Edible Gelatin	35,000,000 lbs.
Photographic Gelatin	7,200,000 lbs.
Pharmaceutical Gelatin	3,600,000 lbs.
Technical Gelatin	4,500,000 lbs.
Total U. S. Consumption	50,300,000 lbs.

This remarkable growth of the gelatin industry has developed in response to a growing need and to the general recognition on the part of industry of the value and uses of gelatin.

What Is Gelatin?

Gelatin is defined in the U. S. Pharmacopoeia as "A product obtained by the partial hydrolysis of collagen derived from the skin, white connective tissue, and bones of animals."

It is not being facetious to point out that gelatin is not manufactured from the horns and the hooves of animals. The fact is that horns and hooves do not contain collagen. They are composed principally of keratin and this protein does not hydrolyze to produce gelatin. The principal raw materials used in gelatin manufacture are ossein, splits, calfskin, and porkskin.

Ossein is produced from bones, principally of beef cattle and water buffalo. The bones are crushed and treated with dilute hydrochloric acid which extracts the mineral constituents. It is interesting to note in passing that the crushed bones of water buffalo, purchased in India and Pakistan, are shipped to Belgium where the bones are converted to ossein. The reason for this is that the costs of labor and hydrochloric acid are low in Belgium. After the minerals are extracted from the bones, the ossein is dried and shipped to the United

States. There is some production of ossein in this country, but it is relatively small.

The second class of raw material consists primarily of splits and calfskin. When hides are removed from cattle, they are run through a splitting machine. The outside of the hide, which is marked with the characteristic grain, is used for the manufacture of leather. This is the so-called "top grain" product. The inside portion of the hide which does not contain the grain is known as a "split" and may be obtained in the form of fresh splits, dried splits, and cured or pickled splits.

The third type of raw material is porkskin. These skins are stamped with the seal of the United States Bureau of Animal Industry, and as soon as they are removed from the animal, are chilled and frozen. The gelatin manufacturer receives them in the frozen form.

The production of gelatin starts with the refinement and conditioning of collagen-bearing materials from these various animal tissues. Along with collagen, small amounts of minerals, fats, albuminoids, mucopolysaccharides, and other non-collagen material are present in relatively small amount. The removal of these extraneous materials by chemical and physical treatment leaves a purified collagen, swelled to several times the original volume by the pretreatment.

Pretreatment Methods

The oldest method of pretreatment consists of liming and washing. Ossein, splits, and calfskin are usually so handled. The period of liming in a strong solution of calcium hydroxide extends over several weeks, and because the pH is high, considerable water is absorbed and swelling results. In this swollen condition, most of the non-collagen fraction is removed. Following liming, washing is carried on in large wash mills in running water, further purifying the raw material.

Porkskins, after thawing and washing, are soaked in dilute solutions of mineral acids such as hydrochloric, phosphoric, or sulphuric. In this process swelling takes place at a rapid rate because of the low pH, and after the skins are properly swelled they are washed again in running water to remove all of the acid not combined with the collagen.

From this point on, all three types of raw materials are processed in very much the same way. The conditioned raw material is extracted with warm water and the dilute gelatin solutions are filtered, concentrated in

* Atlantic Gelatin Division, General Foods Corporation, Woburn, Massachusetts. Received 18 February 1953.



Fig. 1. Dry skins and ossein are stored in warehouses such as this until needed for the extraction of gelatin. Other types of raw materials require refrigerated storage. Still others are processed immediately upon receipt.

vacuum evaporators, and then filtered again. The concentrated clarified solutions are run onto an endless belt which passes through a refrigerated tunnel where the solutions congeal to a firm jelly sheet. The sheet of gelatin, as it emerges from the tunnel, is cut into strips of convenient size to fit the drying nets which are made of coarse wire net of a stainless alloy. Stacks of these nets are then conveyed to the drying tunnels. Here, warm dry air that has been freed from dust is forced over the moist gelatin sheets until they are dry. After removal from the drying tunnel, the long narrow strips of dried gelatin are introduced to the breaking machines and from there to the grinders, screens, mixers, and into the final container.

A recent addition to the Woburn plant equipment is a continuous dryer. Immediately after the second and final filtrations, the concentrated gelatin solution is pumped through votators which are cooled by refrigeration. In these units a reduction in temperature from 110F to 70F solidifies the gelatin and the resulting jelly is forced through a perforated plate, emerging in the form of "noodles" which gives the jelly a tremendous surface area. These noodles are conveyed to a stainless steel wire mesh belt and are evenly distributed at a depth of three inches. The belt moves slowly through the first compartments of the dryer, and sterile conditioned air at approximately 20% relative humidity is passed through the bed of noodles five times. In this operation, 150,000 cubic feet of air is circulated each minute. The gelatin is in this first conditioned section about one hour, after which it is dry enough so that the noodles can be broken and redistributed on the second section belt at a depth of about 12 inches. In the second section, filtered warm air is used to complete the drying. The gelatin is in the second section about five hours, giving a total drying time of about six hours. At the conclusion of the second drying period the noodles are again broken and fed in an air conveying system directly to the grinder where the dry gelatin is reduced to the proper mesh, screened, and packed. This entire operation is automatic.

The entire procedure is supervised by a corps of laboratory workers who check representative samples of each individual batch for jelly strength or Bloom, for viscosity, pH, odor and flavor, clarity, color, bacteria, ash content, and all of the usual pure food standards. The individual lots can then be combined by careful blending to produce standard grades of gelatin well suited for each particular use.

Jelly strength is determined by means of the Bloom Gelometer, a specialized type of penetrometer. The Bloom reading is the number of grams required to force a one-half-inch diameter plummet of special design 4 millimeters into a jelly of 6-2/3% gelatin concentration chilled for 17 hours at a temperature of 10C. Viscosity is determined in an Ostwald type pipette on a 6-2/3% solution of gelatin at 60C. The number of seconds required for the sample to flow through the pipette by mathematical calculation is expressed in National Millipoise units. Electrometric methods are used for pH determination.



Fig. 2. After careful conditioning of raw materials, the gelatin is extracted in warm water and the dilute gelatin solutions are subjected to filtration, purification, and vacuum concentration.

Importance of Sanitation

In the manufacture of gelatin a paramount consideration is sanitation. Gelatin is a good medium for the growth of bacteria and molds. As a result, in former times gelatins were produced with relatively high bacteria counts. The industry has made remarkable strides during the past quarter of a century, however, and today gelatins are produced with bacteria counts considerably lower than the standards for Grade 'A' Milk. As a matter of fact, most lots of gelatin shipped by the major factors in the industry are sterile or essentially so. Examining gelatins for the presence of coliform or liquefying organisms is routine, and pure food gelatins should show negative in every case. Fortunately, pathogenic organisms are of little consequence in the gelatin industry due to the fact that, if present in the raw material, they are killed during the early steps of processing. It is a point of pride in the industry that no instances of food poisoning due to gelatin are recorded in the literature.

To bring about this condition, it is essential that a

bacteriologist and sanitarian supervise the layout of equipment and manufacturing procedures, constantly checking every point in the process to avoid possible points of contamination.

Non Photographic Uses of Gelatin

In the pharmaceutical field, gelatin is used in the production of hard capsules in which powdered drugs are usually dispensed. It is also used in the manufacture of soft capsules. Examples of these are the many types of vitamin "pills" which are familiar. Gelatin is also used in the manufacture of pharmaceutical emulsions, in the manufacture of pastiles, in the production of suppositories, and in the manufacture of cosmetics.

The use of gelatin as a substitute for blood plasma is currently of great interest and considerable work is currently going on in the gelatin industry and in medical circles. For this use gelatin must be non-pyrogenic and non-antigenic. Special processing under pyrogen-free conditions enables the gelatin manufacturer to produce gelatins meeting these exceptionally high standards.

Technical gelatins are used primarily because gelatin is the best known protective colloid, and most of the technical applications of gelatin embody the protective colloidal principal. Some of the other interesting applications of technical gelatin are the sizing and waterproofing of straw hats of both the male and female variety, and the lamination of silver-plated ribbon where gelatins that are free from sulfide and chloride compounds must be used in order to prevent tarnishing the silver. Technical gelatin is also used for waterproofing fabrics. Finally, technical gelatins are used for sizing the warp when fabrics are woven from synthetic materials such as viscose, acetate, and other similar yarns.

More than half of the edible gelatin used in the United States goes into the manufacture of gelatin desserts. Gelatin for this use must be of high Bloom, must have a good viscosity, and must be clear in solution, light in color and bland in odor and flavor.

The meat packing industry uses considerable quantities of edible gelatin in the production of boned, cooked hams, meat loaves, sausage, head cheese, scrapple, canned hams, and jellied tongues. In the meat packing industry, gelatin must be light in color, clear in solution, bland in odor and flavor, high in jelly strength and viscosity and, of course, low in bacteria.

A considerable quantity of gelatin is used in candy manufacture. Most of this gelatin goes into the manufacture of marshmallow. The baking industry also consumes substantial quantities of gelatin. Considerable quantities of gelatin are used in the production of ice cream and sherbets because it is such an excellent protective colloid. In the canning industry, gelatin is used in the production of madrilene soups such as jellied tomato consomme, jellied aspic, and jellied beef consomme. In addition to a high jelly strength, clarity and a bland odor and flavor, stability under the heat of processing is a very important factor in this particular application. All gelatins will break down when heated in solution at a high temperature over a period of time. Special types of gelatin, however, are available having minimum breakdown under any given processing condition.

Gelatin in the Photographic Industry

In the photographic field, gelatin is used as the principal ingredient by weight in the emulsions that coat photographic film and printing papers. Gelatin is unique in the photographic field because of the following physical properties, all of which are essential in making familiar photographic emulsions: (a) Its ability to melt to a liquid and to revert to a jelly insoluble in cold water on cooling. (b) Its action as a powerful protective colloid. (c) The presence of chemical sensitizers, most of them of unknown composition. (d) Its ability, after the addition of "hardeners", to swell without melting or dissolving in water and then, upon drying, to again form a hard, protective matrix for the silver halide grains.

While the physical properties of photographic gelatin such as Bloom, viscosity, and pH are important since they determine the strength and practicability of the film itself, the most important properties of photographic gelatins, namely the photographic properties, are determined by the presence or absence of very minute traces of substances other than gelatin. These traces of impurities either speed up or retard the photographic process.

In photographic emulsions gelatin is more than a mere colloidal vehicle for applying the sensitized ingredients to film or paper. Because gelatin contains a relatively high proportion of reactive side chains it binds silver ions chemically, as well as many other cations and anions. By keeping this concept in mind a better understanding of the photographic properties of gelatin will result.

Inert Photographic Gelatins

Recently the gelatin industry and the photographic industry have been interested in the development of a basic photographic gelatin, i.e., a gelatin so free from all trace impurities and metals that it is photographically inert. Gelatin produced from acid treated collagen materials is not satisfactory in this respect. Gelatin produced from collagen materials which have been fundamentally changed by the lime treatment do approach this ideal and may be almost completely inert. During the liming pretreatment a good proportion of the active

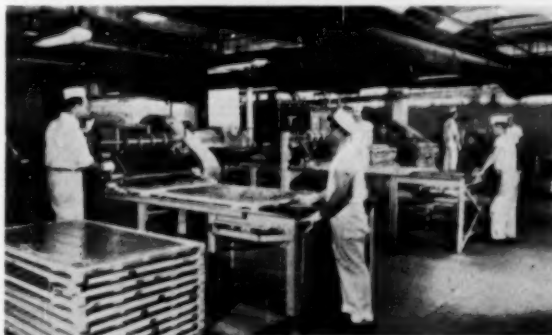


Fig. 3. Continuous sheets of cooled gelatin emerge from the chilling tunnel to be sliced into convenient-size sheets and placed on stainless wire nets for the drying process.

amide groups are removed and it is also apparent that other non-gelatin material is also removed (hyaluronic acid for example). Basic photographic gelatin produced from properly limed stock, while not completely free from active impurities (sensitizers, desensitizers, and restrainers) approaches this ideal and the gelatin industry is today in a position to furnish an almost completely inert basic photographic gelatin.

The idea of a basic photographic gelatin was conceived when it became known that gelatin contains oxidizable and water-soluble sensitizers and other trace impurities such as cold-water-insoluble restrainers. The production of basic gelatin, however, does not solve the problems of the manufacturer of photographic emulsions if he does not possess sensitization methods which can give him all the different types of photographic emulsions which he is called upon to produce. In order to supply him with these various types of emulsion gelatin, it is necessary to blend a great variety of gelatin types which are made from demineralized bone (ossein) and the skins, or part of the skins, of different mammals. In order to develop such complex blends to meet exacting photographic specifications, it is necessary to know what distinguishes these different gelatin types photographically, or to develop chemicals or combinations of chemicals which when added to a basic gelatin can reproduce the photographic properties of the natural gelatin types.

Since the photographic properties of gelatin are so dependent upon trace impurities, a thorough understanding and classification of these impurities is essential. Such impurities may be grouped into three general classes—sensitizers, desensitizers, and restrainers. All of these impurities share with gelatin the property of reacting with silver and gold salts. The silver salts formed with these trace impurities may be either unstable, such as the thiosulphate type; or they may be more stable than the complexes which silver and gold ions form with gelatin itself. Impurities which lead to more stable complexes of silver and gold are the restrainers. They intensify the restraining properties of gelatin and retard the action of the sensitizers without altogether inhibiting it. Therefore, they make it possible better to control the ripening process of the photographic emulsion and to improve its keeping properties.

Since a basic gelatin has been purified and has, therefore, lost its sensitizing and restraining impurities, it is necessary to replace these impurities either by blending with gelatins in very carefully controlled proportions, or by adding synthetic sensitizers and restrainers. Incidentally, sensitizers need not of necessity be compounds containing labile sulphur, nor must the restrainers necessarily be degradation products of non-collagen proteins. The important property in the case of sensitizers is their ability to form electron traps in the silver halide crystals of the emulsion. The function of the restrainers is to

retard the reactivity of the silver or gold ions so that the emulsions do not fog before they reach maximum speed and gradation. A basic gelatin should also be free from metal traces, particularly copper, tin, lead, mercury, and iron; also non-metal traces which interfere with the photographic ripening process and which distort the normal functioning of natural or synthetic sensitizers, restrainers, and reducing substances.

Although much is currently known as to the nature of these trace impurities and their action in photographic emulsions, there is much still to be learned. It is not unlikely, however, that the synthetic approach to the problem of sensitization and its control by synthetic restrainers may eventually result in photographic gelatins superior to those currently being produced by blending various types of gelatin. In order to reach this goal the first step had to be the manufacture of gelatins approaching completely inert or "basic" gelatin. Once this goal had been approached fairly closely it was possible to study experimentally the combined effects of added sensitizers and restrainers, obtaining data that is reliable. Without such a basic gelatin it would be difficult, if not impossible, to interpret the results obtained when restraining and desensitizing substances are added.

Currently, the efforts of the gelatin manufacturer are directed toward improving existing varieties of gelatin types with their various and differing amounts of natural sensitizers and restrainers, and at the same time toward the development of a basic gelatin which will respond—at all times—reliably to the addition of sensitizers and restrainers. It is well to bear in mind however, that gelatin itself—even basic gelatin—is not just another binder or protective colloid, but it also reacts actively with the other ingredients of the emulsion. In this respect, gelatin acts as a basic restrainer or, as older chemists put it, as a filter against fog-producing nuclei. This specific characteristic which results from the active groups in the gelatin molecule itself, is the chief reason why gelatin holds such an important place in the photographic field, and is doubtless the reason why other high polymers have not been able to replace it in photographic emulsions.

Because the requirements of each manufacturer are so very precise, photographic gelatin is sold for the most part on sample. Working samples representing large quantities of gelatin are sent to the manufacturer who tests them in his own particular types of emulsions, after which he either approves or rejects the lot. Because of the exacting nature of this type of business, the gelatin manufacturer must maintain a photographic laboratory that tests every lot of photographic gelatin for its particular properties. The Director of the Photographic Laboratory works closely with the laboratory personnel of the film manufacturer, and thus the requirements of each customer are adequately served.

Kinetics of Development of Liquid Photographic Emulsions

III. Development by N-Methyl-*p*-aminophenol (Metol)*

L. J. Fortmiller and T. H. James

ABSTRACT

The kinetics of development by N-methyl-*p*-aminophenol (Metol) of a dispersion of silver halide grains in dilute gelatin solutions were studied over the pH range of 7.7 to 10.2. The development curve shows a definite induction period in the presence of added bromide, but little or none in its absence. The rate of development increases to a maximum with increasing concentration of sodium sulfite; is proportional to the concentration of Metol; and increases with increase in pH, but not to the same extent as the concentration of ionized Metol increases. It is suggested that the active developing agent is the Metol ion (although un-ionized Metol may show some activity), but the increase in negative charge of the adsorbed gelatin layer with increase in pH prevents the rate of development from increasing in direct proportion to the concentration of the ion. The over-all energy of activation of latent-image development is about 16 kcal/mole at pH 8.1. If the heat of ionization is about 5 kcal/mole, the activation energy is reduced to 11 kcal/mole. The over-all energy of activation of fog formation is 22 kcal/mole at pH 12.4, where no correction for heat of ionization is called for.

PREVIOUS PAPERS of this series have dealt with the kinetics of development of liquid photographic emulsions by members of the *p*-phenylenediamine series¹ and hydroquinone.² The present paper concerns the kinetics of development by Metol (N-methyl-*p*-aminophenol sulfate, Elon[†]), the most widely used member of a third series of developing agents, the *p*-aminophenols. This series represents a type intermediate between the *p*-diaminobenzenes (*p*-phenylenediamines) and the *p*-dihydroxybenzenes (hydroquinones).

Experimental Procedure

The apparatus and general procedure followed in this work are the same as those described in the previous papers.^{1,2} Kodak Elon Developing Agent was used and the silver halide grains were from the same emulsion preparation as before. Unless otherwise indicated, the developer solution contained 30 millimoles of sodium sulfite, 2 millimoles of Metol, and no potassium bromide per run in a total of 500 milliliters reaction volume, and the temperature was 20°C.

Experimental Results

The reaction between Metol and the exposed silver halide, as represented by the growth of the optical density of silver plus silver halide, can be represented to good approximation by a first-order equation over much of the reaction course. Figure 1 shows a first-order plot of $\log(D_{\infty} - D)$ against the time of development at pH 9.0 in the presence of sulfite. A short induction period is indicated by this plot, but it is probable that this largely represents the time required for the pump (about 3 seconds) to bring emulsion containing developer to the observation cell, rather than a true induction period

in the reaction. Other data show, however, that a true induction period exists for development by Metol under proper conditions, particularly when excess bromide is present in the developer.

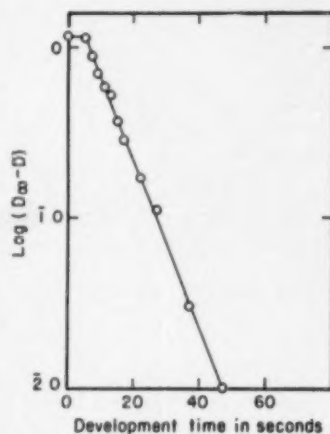


Fig. 1. Typical first-order plot for liquid emulsion developed by Metol at pH 9.0 with 30 millimoles of Na_2SO_3 per 500 ml.

In the subsequent presentation of data, the absolute value of the slope of the straight line obtained by a first-order plot will be taken as one measure of the reaction rate, and will be designated as k . When the slope of this curve is in doubt, two limiting values of k will be given. Reaction rates also will be expressed in terms of the reciprocal of the times required to complete 10 percent and 50 percent of the total reaction. In general, good agreement is obtained between relative rates expressed in the three different ways. The effect of sulfite on development by Metol at pH 9.4 is illustrated by the density-time of development curves in Figure 2. These curves represent sodium sulfite additions of 0, 3, 10, 30, and 80 millimoles per 500 ml. Similar results were obtained at pH 8.1, except that addition of sulfite produces a greater increase, both in rate of increase of density and in the value of the maximum density developed.

The rate of development increases with increasing pH. The dependence of rate upon pH is greater for Metol than

* Communication No. 1543 from the Research Laboratories, Eastman Kodak Company, Rochester 4, New York. Received 25 February 1953. Part I. Development by Derivatives of *p*-Phenylenediamine appeared in the November 1951 issue. Part II. Development by Hydroquinone appeared in October 1952.

† Elon is a trade name copyrighted by the Eastman Kodak Company for this agent.

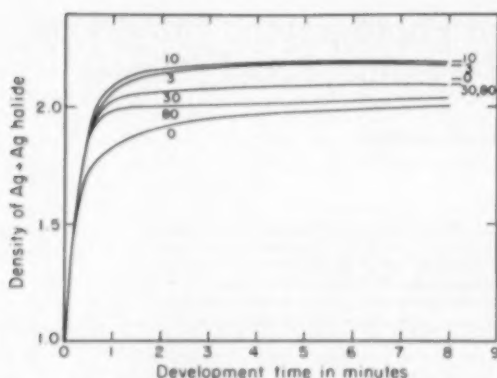


Fig. 2. The effect of adding Na_2SO_3 . Figures on the graph indicate millimoles added per 500 ml.

for the *p*-phenylenediamines,¹ but is smaller than for hydroquinone² in the same pH range. Figure 3 gives a plot of the log rate values against the pH for Metol. The curves representing the three different measures of rate are substantially parallel, showing that the relative pH-dependence does not vary with the particular method chosen to represent rate. Figure 3 also shows the variation in concentration of un-ionized Metol and ionized Metol as a function of pH. The dissociation constant used to calculate these concentrations is that given by Cameron,³ and has the value 4×10^{-11} at 20°C. It is seen that the concentration of ionized Metol increases more rapidly than the rate of development.

The dependence of rate of development upon the Metol concentration was determined at pH 8.9, using 50 ml of 0.01 M borax as buffer, and adjusting the pH by additions of small amounts of potassium hydroxide. Figure 4 shows a plot of the rate of development against the Metol concentration. The experimental points are represented satisfactorily by a straight line, showing that the rate is proportional to the Metol concentration.

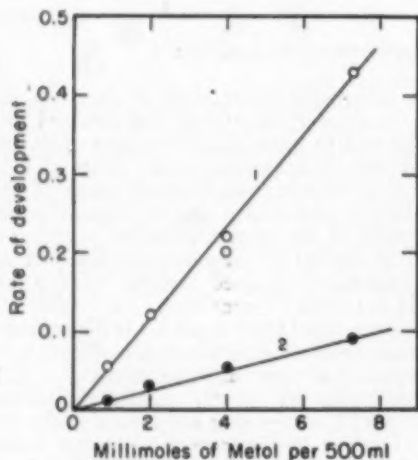


Fig. 4. Development rate as a function of Metol concentration. 1. Rate = $10k$. 2. Rate = $1/t$ for 50 percent of development.

Figure 5 shows the effect of adding 0, 0.5, 2, and 8 millimoles of potassium bromide per 500 ml of solution at pH 9.0. The induction period increases with increasing bromide ion concentration, and the rate of development decreases.

The effect of temperature upon the rate of development by Metol at pH 8.1 was studied between 11 and 30°C. Three development rates were determined for each temperature, namely, the rate constant k , the reciprocal of the time in seconds required to complete 50 percent of the total development, and the maximum slope of the density-time curve corrected for any variation in D_{∞} . The logarithms of these rates, plotted against the reciprocal of the absolute temperature, gave satisfactory straight lines. The over-all activation energies determined from these Arrhenius plots are given in Table I.

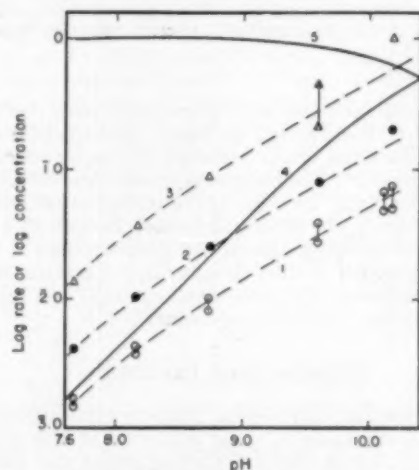


Fig. 3. The pH-dependence of the rate of development by Metol compared with the pH-dependence of the ionization of Metol. 1. Rate = k . 2. Rate = $1/t$ for 50 percent of development. 3. Rate = $1/t$ for 10 percent of development (uncertain above pH 9 because of short times of development). 4. Relative concentration of Metol ion. 5. Relative concentration of un-ionized Metol.

The values vary from 15.4 to 16.7 kcal/mole. In the early stages of development, the energy may be somewhat lower, but the accuracy of the measurements in this region is not sufficient to give reliable figures.

The temperature-dependence of fog formation in development of unexposed emulsion at pH 12.4 was determined over the same temperature range. An unusual behavior was observed in these experiments. The optical density of the silver plus the silver halide increases to a maximum as development proceeds, and then falls off considerably. Because of this unorthodox behavior, developed-silver mass determinations and diffuse-silver density determinations were made on samples of emulsion taken at intervals during development and fixed out by the method previously described.¹ The amount of silver and the diffuse-silver densities both increase with development time until all of the silver halide is reduced. However, the relative rate values determined for the various temperatures using the silver

Table I

ACTIVATION ENERGIES OF IMAGE DEVELOPMENT AND FOG FORMATION BY METOL

Development of:	pH	Rates used	Temp. Coef.	Energy of Activation
Image	8.1	1/r (50%)	2.46	15.4
Image	8.1	Max slope	2.51	15.7
Image	8.1	k	2.66	16.7
Fog	12.4	1/r (1 mg Ag)	3.82	22.9
Fog	12.4	1/r (.2 mg)	3.70	22.4
Fog	12.4	Max slope	3.22	20.0
Fog	12.4	k	3.48	21.3

mass and silver-density curves agree reasonably well with the relative rates determined from the maximum slopes of the density of silver plus the silver halide curves. These values are listed in Table I. The measured activation energy of fog formation varies from 20.0 to 22.9 kcal/mole, depending on the method used to express the reaction rates.

Discussion

The rate of development and the maximum density obtained with Metol at a given pH increase with increasing sulfite concentration, pass through a maximum, and then decrease. This behavior is qualitatively the same as that observed with the *p*-phenylenediamines,¹ and the cause is probably the same. The oxidation product of Metol evidently interferes with the course of development, and it probably does this by attacking and destroying latent-image centers in some grains having relatively long induction periods. The sulfite effectively prevents the formation of this oxidation product, or removes it before it can exert its detrimental effect. The action of sulfite is less noticeable at higher pH because the stability of the oxidation product is decreased by increase in pH. Alkaline decomposition of the oxidation product serves the same purpose as removal by reaction with sulfite. The decrease in rate and density observed at high sulfite concentrations probably is a consequence of the solvent action of sulfite on silver bromide.

The rate of development is directly proportional to the concentration of Metol at constant pH. The rate increases with increasing pH, but the increase is less than proportional to the concentration of ionized Metol. The concentration of the ion increases about 200-fold from pH 7.7 to 10.2, but the rate increases only about 40-fold. It may be that both ionized and un-ionized Metol are active in development, but the shape of the rate-pH curve cannot be accounted for quantitatively by a linear combination of rates for development by the ion and by the un-ionized molecule. However, the rate of development by *p*-phenylenediamines increases with increasing pH, and this has been attributed to alkaline decomposition of a retarding oxidation product. An oxidation product of Metol exerts a similar retarding action on development, as evidenced by the action of sulfite, and this may influence the quantitative dependence of rate upon pH.

It is clear, however, that the Metol ion does play an active role in development, even if the un-ionized form is capable of developing action, and the specific rate of reaction of the ion must be considerably greater than that of the molecule. The dependence of rate upon pH is

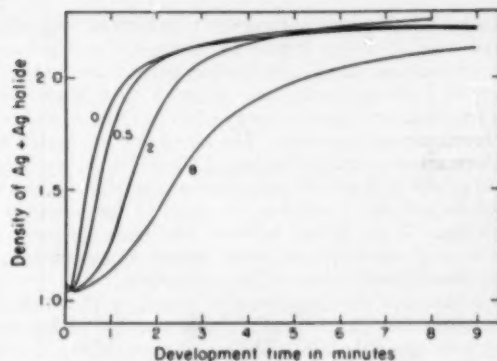


Fig. 5. The effect of adding KBr. Figures on the graph indicate millimoles added per 500 ml.

greater for Metol than for the *p*-phenylenediamine derivatives studied, whereas the evidence indicates that removal of retarding oxidation product by sulfite is much more efficient during development by Metol than by the *p*-phenylenediamines. Hence, it is unlikely that a change in stability of the oxidation product could account completely for the increase in rate with pH. Moreover, the marked dependence of the induction period upon bromide ion in Metol development, and the fact that development is accelerated by quaternary salts such as α -picolinium- β -phenylethyl bromide, indicate that the ion is an important factor in determining the rate of development.

A variation of the charge effect may enter as a modifying factor in determining the variation of rate with pH. The silver halide grains are surrounded by a layer of adsorbed gelatin. Gelatin possesses a net negative charge in alkaline solution, and the magnitude of this charge increases with increasing pH in the region between 7.7 and 10.2, as indicated by the titration curve,⁴ adsorption of cationic dyes,⁴ and cataphoretic studies.⁶ The negative charge of the gelatin impedes the diffusion of negatively charged developing agents through the gelatin layer⁶ because of electrostatic repulsion, and the impedance should increase with increasing charge of the gelatin. Likewise, the charge should act to decrease adsorption of the ionized Metol. In effect, this results in a decrease in the relative concentration of the ionized developer at the grain surface. Hence, the increase with pH in the concentration of Metol ion at the grain surface where development takes place will be smaller than the calculated increase in ion concentration in solution, and the change in development rate will be less than proportional to the change in concentration of the ion in solution. The gelatin layer involved in the present experiments is the layer of gelatin adsorbed by the silver halide grains. Therefore, it appears possible to account for the pH-dependence of development by Metol solely on the basis of the activity of the ionized form, but we cannot definitely rule out participation of the un-ionized form in the absence of quantitative information on the charge effect of the gelatin.

The overall energy of activation of development of the exposed silver halide at pH 8.1 is about 16 kcal/mole. If the Metol ion is primarily involved in the reaction, this value should be corrected for the heat of ionization

of the hydroxyl group. Data for this heat of ionization are not available, but it may be assumed that the value is about the same as that for the ionization of a hydroxyl group in hydroquinone, i.e., about 5 to 6 kcal/mole. This leaves an activation energy of 10 to 11 kcal/mole for the development reaction. The energy of activation for fog formation is much higher, 22 kcal/mole, as determined at pH 12.4 where ionization of the Metol is nearly complete and no correction for heat of dissociation is necessary. Thus, Metol behaves like hydroquinone, in that both show a much lower energy of activation of image development than of fog formation.

The fact that the fog curves obtained by plotting the silver plus silver halide densities against time of development pass through a maximum and then decrease, even though the silver mass continues to increase, suggests a coagulation of silver particles as reaction proceeds. Such a reversal of the density curve was not observed in

latent-image development by Metol, or in latent-image or fog development by hydroquinone. It appears probable that numerous fog centers are formed on each grain in the reaction with Metol, and that these coalesce as they increase in size. This explanation implies that the fog centers formed at pH 12.4 are much more numerous than the latent-image centers formed by exposure to light.

References

1. L. J. Fortmiller and T. H. James, *PSA Journal Section B (Phot. Sci. and Technique)*, Vol. 17B, p. 102 (1951).
2. L. J. Fortmiller and T. H. James, *PSA Journal Section B (Phot. Sci. and Technique)*, Vol. 18B, p. 76 (1952).
3. A. E. Cameron, *J. Phys. Chem.*, Vol. 42, p. 1217 (1938).
4. S. E. Sheppard, R. C. Houck, and C. Dittmar, *J. Phys. Chem.*, Vol. 46, p. 158 (1942).
5. W. Reinders and W. M. Bendien, *Rec. trav. chim.*, Vol. 47, p. 977 (1928).
6. T. H. James, *J. Chem. Phys.* Vol. 12, p. 453 (1944).

LIGHT-BALANCING FILTERS FOR COLOR PHOTOGRAPHY*

L. D. Clark

ABSTRACT

It is not feasible for the manufacturers of light sources of various types used for color photography to make them all like daylight in spectral quality so that only daylight types of film are required. Neither is it feasible for the manufacturers of photographic materials to make a different color material balanced for each of the light sources used for color photography. The usual practical compromise is to make each kind of color film in two types, one balanced for daylight and one for some other type of light. It therefore becomes necessary to use filters in order to modify the other light sources to match those for which the films are specifically balanced. For instance, Kodachrome Film, Type A, balanced for photoflood lamps, requires a filter for use with photoflash.

When the light source approximates a blackbody in its spectral energy distribution, the problem can be approached from the standpoint of energy conversion from one blackbody distribution to another or to daylight distribution. When the light source to be modified gives a discontinuous spectrum entirely unlike a blackbody or daylight, as in the case of fluorescent lamps, it is usually impossible to obtain a filter which will convert the energy distribution to that of a blackbody, and a different approach must be used. This approach is a matter of obtaining a proper balance among the responses of the three layers of the color film by controlling, with filters, the relative amounts of energy reaching the film in each of the regions of the spectrum to which the three layers are sensitive.

In addition to a discussion of these two types of light-balancing, the tests used in these Laboratories for determining the choice of filters are described. Filters developed for use with a wide variety of light sources are discussed.

IN ORDER to obtain satisfactory color rendition with a subtractive color process, there must be a correct relationship between the relative sensitivities of the emulsions which control the dyes in the film and the spectral distribution of the energy which is incident on the objects in the scene. The ideal relationship exists when the dyes deposited have, in combination, a spectral transmittance such that the picture creates in the mind of the observer the same impression of color as was obtained from viewing directly the object photographed. Since daylight is our primary light source, it would be very convenient if all other light sources were made to provide

the same spectral distribution of energy as daylight. We should then need only daylight types of color film. Actually, few sources of light resemble daylight sufficiently closely to permit the use of daylight-type film directly. It is not feasible, however, for the manufacturers of photographic materials to make a different color material balanced for each of the light sources used for color photography. The practical compromise which has been reached is to make most color films in two types, one balanced for daylight and the other for some other type of light source. It therefore becomes necessary to use filters in order to modify the other light sources to match those for which the films are specifically balanced. For instance, Kodachrome Film, Type A, balanced for photoflood lamps, requires a filter for use with photoflash.

* Communication No. 1516 from the Research Laboratories, Eastman Kodak Company, Rochester 4, New York.

Let us then consider the characteristics of the various light sources used for color photography. First, it should be readily understood that if it were possible by suitable filtering to transform the spectral energy distribution of each source into an exact copy of the energy distribution of the source for which the film is balanced, then the match between the pictures taken with the reference source and with the filtered source would be perfect for any given film. Since it is unlikely that this objective will be attained, we must resort to the best compromises available. Two approaches to the problem will be considered here: one for sources approximating a blackbody in spectral energy distribution, the other for sources giving a discontinuous spectrum entirely unlike a blackbody.

Energy-Conversion Filters

An incandescent solid, such as a tungsten filament, emits radiant energy at all wavelengths in a regular manner which depends in a definite way on filament temperature. It is well known that as the temperature of the filament increases, its color becomes more bluish. This means that the peak of the energy-distribution curve shifts toward the short-wavelength end of the spectrum.

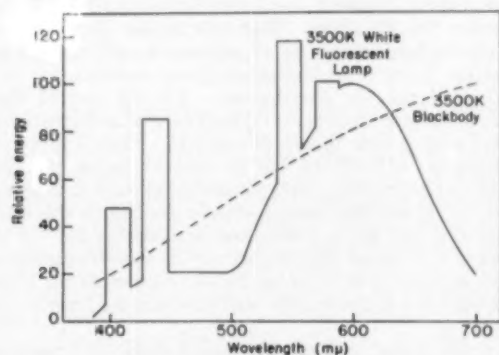


Fig. 2. Spectral energy distribution of the radiation from a 3500 K white fluorescent lamp compared with 3500 K blackbody radiation.

A blackbody behaves in a manner similar to the tungsten filament just described. It is used as a standard of reference because it is rigidly definable and follows definite laws of radiation. The characteristic of a blackbody which gives it its name is that it has zero reflectance. In other words, it is black when cold.

For any particular temperature of a blackbody, there is a definite and well-known spectral energy distribution. Figure 1 shows a series of blackbody curves ranging from 2600 K to 8000 K. These curves represent relative values and have been arbitrarily adjusted for convenience to intersect at 560 millimicrons, the point of maximum luminous efficiency for the human eye. For comparison, the spectral energy distribution of daylight is shown by a broken line.

The color-temperature designation has come into use by those who are concerned with light sources and color photography. Certain dangers and pitfalls should be mentioned in connection with the term. The color

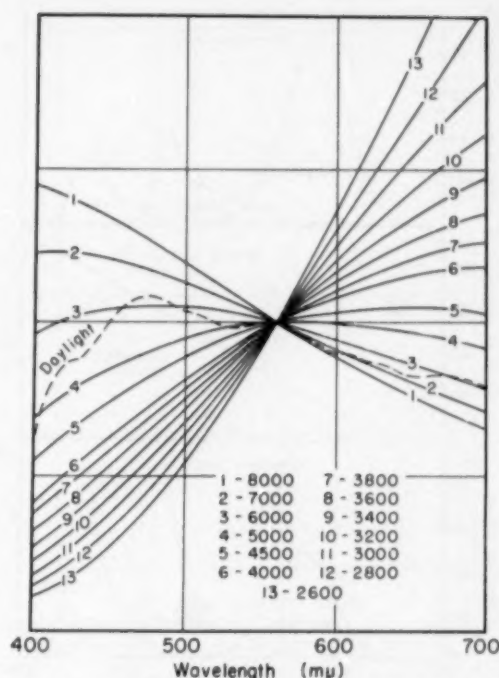


Fig. 1. Blackbody radiation curves. Light-balancing filters will convert light sources from one to another of these energy distributions.

temperature of a source is the temperature of a blackbody having the same color as the source. This does not mean that the source has a blackbody energy distribution. It means that to an average observer its color is the same as the blackbody. For instance, the daylight curve, Figure 1, is quite different from any of the blackbody distributions shown. Yet the color of daylight is almost exactly the same as the color of the radiation from a blackbody at about 6500 K. Since daylight has the same visual appearance, that is, the same color as a 6500 K blackbody, then by the definition given above the color temperature of daylight is about 6500 K. However, the photographic effect of daylight and of a blackbody at 6500 K is not the same.

Figure 2 shows a more extreme example. Both the blackbody source and the fluorescent source have a color temperature of 3500 K. This means that they look alike in color. Furthermore, if these two sources were to be used for viewing strictly neutral objects (nonselective absorbers), the visual results would be the same. But, if we introduce selective absorbers, that is, colored objects, into the scene, the visual appearance of the scene illuminated by the two different sources may differ markedly because of the different spectral energy distributions.

Although these two sources are visually matched, photographically they may differ because of the difference between the spectral sensitivity of the film and that of the eye. Thus, colored photographs taken with the two sources will differ not only in the rendition of the colored objects, but in the rendition of the gray scales. Consequently, while a color-temperature designation of a fluorescent lamp is in keeping with the present definition

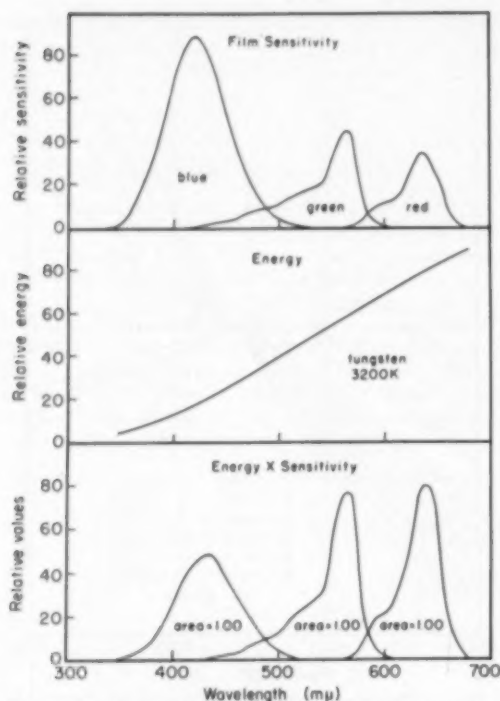


Fig. 3. Spectral sensitivity of film balanced for 3200 K tungsten illumination.

of color temperature, that designation is not very useful to a butcher in predicting how the meat in his display counters will look, or even less so to a photographer in predicting how his color pictures will look.

More recently, lamp manufacturers have dropped the use of color-temperature designations in connection with fluorescent lamps, recognizing that such designations are misleading.

It is the spectral energy distribution, therefore, and not the color temperature, which is the more significant variable in taking color pictures or in viewing colored objects.

The term "color temperature," however, is difficult to escape in the printed literature dealing with this subject. As long as the sources which are being considered give a blackbody spectral energy distribution, or nearly so, such as tungsten, flash bulbs, etc., the use of the term color temperature is a convenience and will do little harm if it is clearly understood that the spectral energy distribution is the important variable.

Figure 3 shows the spectral sensitivity of the three layers of a typical color film which is balanced for a tungsten lamp operated at 3200 K. The 3200 K blackbody curve also shown here represents the spectral energy distribution to which lightbalancing filters must convert the spectral energy distribution of other sources if they are to give identical photographic results.

Figure 4 shows a set of seven filters, which are required to convert the radiation from blackbodies of higher temperature to a 3200 K blackbody distribution. These conversions progress in 100 K steps, beginning with a conversion of 3300 K to 3200 K distribution. The Eastman

Table I

KODAK LIGHT-BALANCING FILTERS

Present Designation	Former Designation	Change in Blackbody Temperature, °K	Net Change, °K
82C	CC6	2800 to 3200	+400
82B	CC5	2900 to 3200	+300
82A	CC4	3000 to 3200	+200
82	CC3	3100 to 3200	+100
81	CC13	3300 to 3200	-100
81A	CC14	3400 to 3200	-200
81B	CC15	3500 to 3200	-300
81C		3600 to 3200	-400
81D		3700 to 3200	-500
81EF		3850 to 3200	-650

Kodak Company markets a set of filters to accomplish this same group of conversions except that 6 and 7 have been replaced by a single filter which converts from 3850 K to 3200 K. These Kodak Wratten Filters are designated as the No. 81 series, from 81 to 81EF. Figure 5 illustrates the degree to which the calculated curves of Figure 4 have been matched by the spectral transmittance curves of the actual filters. The curve for Filter 81C is shown compared with the corresponding calculated curve. Figure 6 shows the curves of all the Kodak Wratten No. 81 series. Figure 7 shows the 82 series, which are bluish instead of yellowish and convert the radiation from blackbodies of lower temperature to a 3200 K blackbody distribution. The 81 and 82 filter series are a more extensive counterpart of a discontinued series, with a new system of naming. Table I gives the designation of each of the 81 and 82 series of light-balancing filters, the energy conversion each is designed to perform, and the name formerly applied to the filters in the original series. The new designation has the advantage that these light-balancing or energy-conversion filters will not now be as easily confused with the color-compensating filters which will be discussed later in this paper.

At this point, it should be noted that, as a practical matter, the 81 and 82 filter series can be used for other conversions of approximately the same number of degrees but ending at a different final temperature, if the final temperature is not too far different from 3200 K. For instance, Filter 81C is used for converting flash lamps which approximate a 3800 K blackbody distribution to a 3400 K distribution, for which Kodachrome Film, Type A, is balanced. Filter 81C is specifically intended for converting from a 3600 K to a 3200 K distribution. The ideal filter-transmittance curves for these two different conversions, each covering a 400 K change, do not differ appreciably.

Filter Recommendations

The published recommendations for the choice of filters for any particular light source and film combination are based on picture tests. Each set of test pictures is accompanied by a comparison picture taken with the light source for which the film is balanced. Care is taken to hold all factors in each case, except the light source differences under test, as nearly constant as possible between the test pictures and the comparison picture.

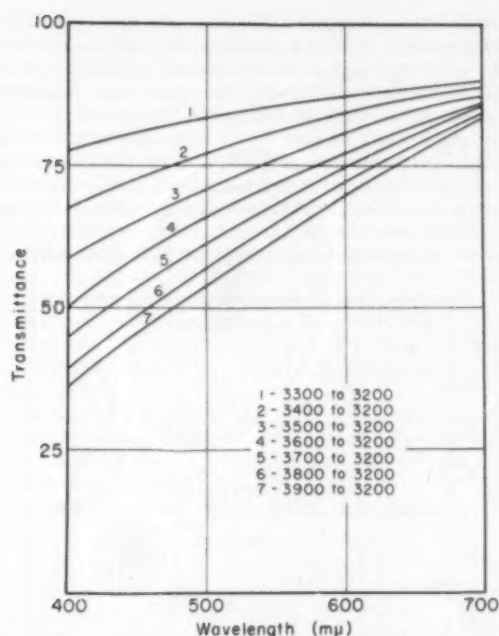


Fig. 4. Calculated filters for blackbody energy conversion.

Noticeable differences between the density levels of the pictures are avoided by proper selection of exposures. The number of sources, their angular extent, and their positions are kept as nearly the same as possible between exposures of the test and comparison pictures.

For tests of flash lamps, a single tungsten lamp in a reflector, carefully calibrated in the reflector for color temperature, is used for the comparison picture in order to correspond with the single flash lamp in a reflector in the same position.

The problem of differences in color due to reciprocity-law failure enters at this point. The following example illustrates what this means: Two pictures are taken of the same subject on the same color film, using the same quality of illumination. The time of exposure for one is 2 seconds; for the other, $\frac{1}{50}$ of a second, a corresponding adjustment in the intensity of the illumination falling on the film being made by means of aperture adjustment or number of lighting units. If there is no reciprocity-law failure inherent in the film, the two pictures will be identical, since the exposures (intensity \times time) were equal and the light source was the same for both. However, if there is failure of the reciprocity law, and if there is a different degree of failure for one of the layers of the color film than for another, color differences will result.

Since the intensity of a single tungsten source is considerably lower than that of a flash lamp, it is normally necessary to use longer exposure times for the tungsten pictures than for the flash-lamp pictures. In some cases, this has led to sufficiently large reciprocity effects to confuse the choice of filters.

Usually the choice of filters based on picture tests agrees with the choice predicted by energy-conversion considerations. However, tests with Kodak Ektachrome and Kodachrome films have, in some cases, led to a filter

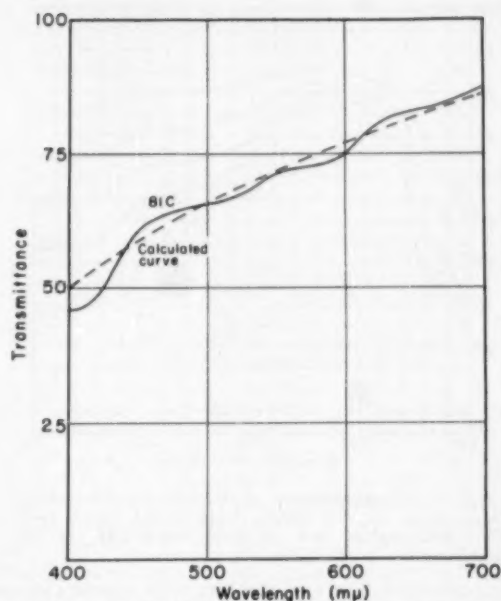


Fig. 5. Calculated versus actual filter for converting blackbody distribution at 3600 K to 3200 K.

choice differing from the choice predicted by energy-conversion considerations by one step in the 81 filter series. It is quite probable that the discrepancy between the predicted conversion and the one selected from the picture tests in such cases is due to a reciprocity-law-failure effect. The speed of the sheet films and the picture-taking conditions of the test are such that the tungsten exposures are made at an exposure time of one second compared to $\frac{1}{50}$ of a second for the flash pictures. This difference in exposure time (a ratio of fifty to one) means that any reciprocity-law failure which may exist in any

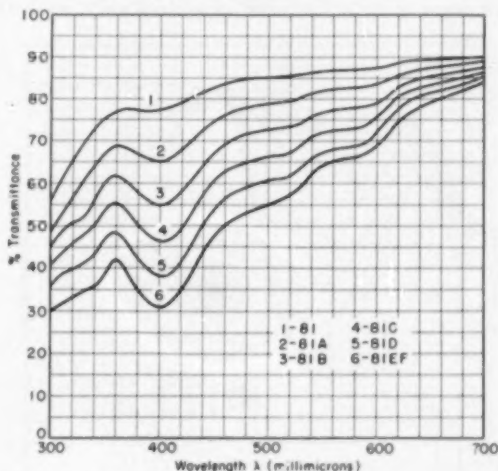


Fig. 6. Transmittance of Kodak light-balancing filters, series 81, for energy conversions which lower color temperature and maintain blackbody spectral distribution.

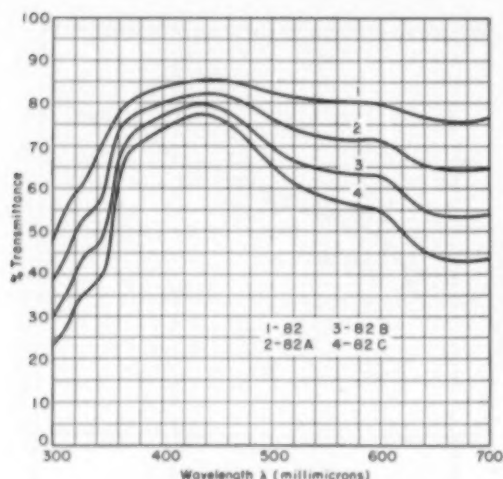


Fig. 7. Transmittance of Kodak light-balancing filters, series 82, for energy conversions which raise color temperature and maintain blackbody spectral distribution.

of the emulsion layers of the film will appear as color differences in the picture even if the light sources are spectrally matched. This difference in exposure times is difficult to avoid in regular photographic practice, as well as in these tests, because of the great difference in intensity between flash lamps and tungsten lamps. Since this is so, it is not considered advisable to try to eliminate the reciprocity effects from the tests, but rather to let the filter recommendations help to correct for reciprocity-law failure as well as make the required energy conversion.

Color-Correction Filters

The second approach to light-balancing applies when the source to be corrected has an irregular spectral energy distribution quite unlike that of a blackbody, as in the

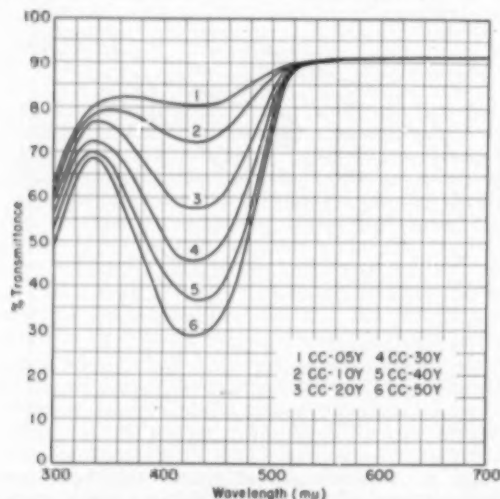


Fig. 9. Transmittance of Kodak yellow color compensating filters.

case of fluorescent lamps. Fluorescent lamps, in addition to the energy emitted in a continuous spectral distribution by the various phosphors in the fluorescent coating of the lamps, emit energy at certain spectrum lines characteristic of the mercury arc which excites the phosphors.

The ideal result of filtering in this case would be an exact energy conversion as in the case of flash lamps, but it is impossible to produce a filter with a spectral transmittance which will compensate for the irregularities of spectral emission of such a source. We must be content, therefore, with obtaining a balance of response among

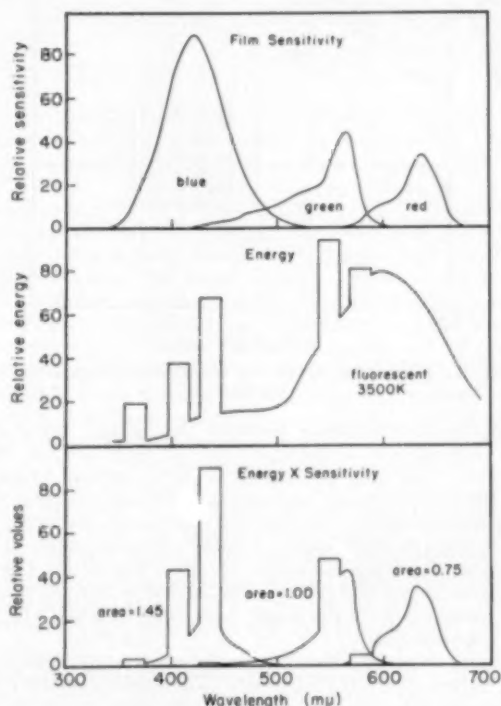


Fig. 8. Condition requiring color compensating filters—film balanced for 3200 K tungsten illumination used with 3500 K fluorescent source.

the emulsion layers which will give the best possible color rendition, knowing that not all the colors produced with the reference source can be exactly duplicated with the filtered fluorescent source.

The situation is illustrated by Figures 3 and 8. Figure 3 shows the spectral sensitivity of a film whose three layers are balanced for a 3200 K tungsten source, the spectral energy distribution of which is shown immediately below the sensitivity curve. The bottom curve shows the product of energy and sensitivity. If the areas under these curves are equal, as in Figure 3, a neutral balance for some one step on a gray scale is indicated.

Figure 8 represents a fluorescent lamp used with the same film. In order to have the same neutral balance as in the previous case, it is necessary to have equal areas under the lower curves. Since these areas are not equal, the gray-scale step, which was neutral before, will not be in this case.

The problem here is to absorb some energy by means of filters in the spectral regions which have too much energy. This is not essentially different from what happens in the energy-conversion cases, which were discussed before, except that the resulting product curves are irregular in shape. Even though the gray scale has been brought by means of filters to the same balance as for the 3200 K blackbody, a colored object may have a spectral reflectance such that it will not be rendered the same in the two cases. To determine what further adjustment in filtering is required, we therefore resort again to picture tests. The picture chosen as most pleasing may, in a particular case, match more closely the check picture in the flesh tones than in the gray areas. A compromise must be made in which the emphasis is placed on the correct rendition of the more important or more critical colors.

In order to have more degrees of freedom in adjusting the energy distribution in such cases, it is desirable to have a set of filters to control the energy in each of the three primary spectral regions separately. The Kodak Color Compensating filters serve this purpose. They

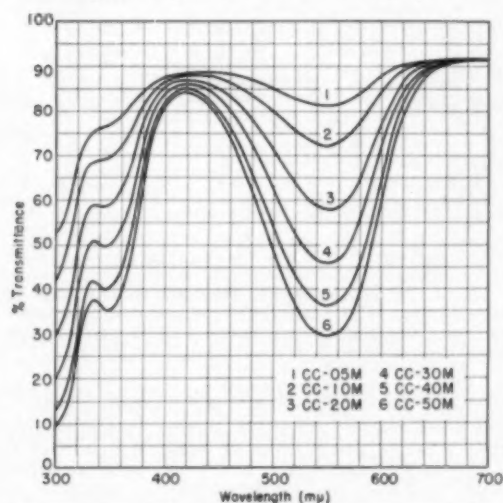


Fig. 10. Transmittance of Kodak magenta color compensating filters.

consist of a series in each of the three subtractive dyes—yellow, magenta, and cyan—and in blue, green, and red, which are combinations of pairs of the subtractive dyes. Figures 9-11 show spectral transmittance curves of the first three of these filters. Each filter is designated in terms of the peak density in the region where the absorption is greatest in the visible region of the spectrum. This set of filters replaces a discontinued set which was spaced and named differently.

Figure 12 shows how the new Kodak CC Filters are related to the older ones. The old filters were spaced by doubling the dye concentration in each succeeding member of a series. This led to large intervals between the darker members of the series, as shown in the graph, and unnecessarily small intervals between the lighter members. The filters in the new series are spaced with respect to the density at the wavelength of maximum absorption, and these steps are the same for each of the

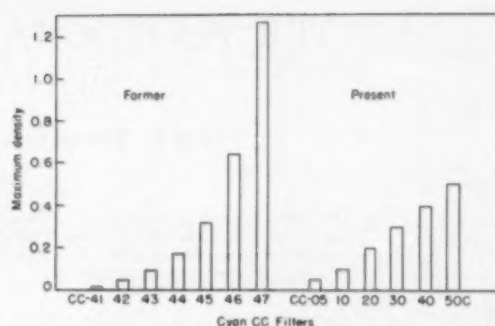


Fig. 12. Density comparison of former Kodak series of cyan filters with present cyan filters

series. As the figure shows, there are five filters spaced at 0.10-density intervals, with an additional 0.05 filter at the light end of the series. The names of the filters are systematic. They indicate in each case the maximum density and the color series to which each filter belongs. Such an arrangement permits a flexibility in choosing the proper combination for any purpose. These filters are useful in many ways besides the light-balancing function described here.

Before concluding this discussion of light-balancing filters, Kodak Wratten Filters Nos. 80, 85, and 85B should be mentioned. Filter 80 is for use in taking photo-flood pictures with daylight-type films, Filter 85 is used for taking daylight pictures with Kodachrome Film, Type A, and Filter 85B is used for the same purpose with Type B films. These filters are not true energy-conversion filters, but instead they balance the spectral energy distribution of the source to the sensitivity of the film, as in the case of the Kodak CC Filters.

The pertinent information on all the filters mentioned here is given in the Eastman Kodak Company publication, "Filter Data for Kodak Color Films." A complete table of recommendations for filter choice is also given in this booklet.

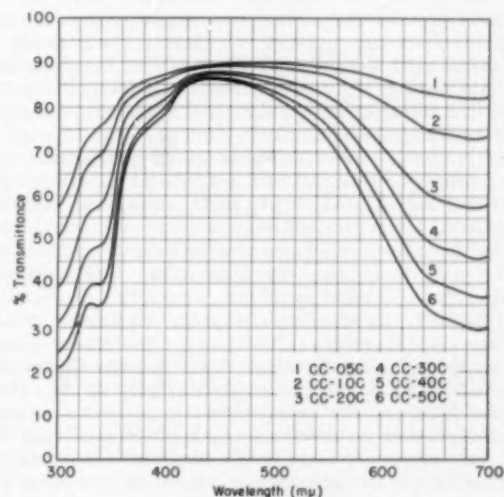


Fig. 11. Transmittance of Kodak cyan color compensating filters.

BETTER PHOTOGRAPHIC LENSES FOR THE SIGNAL CORPS

John C. Thomas, Jr. and Carroll W. Arford*

ABSTRACT

The Signal Corps has prepared procurement information for 58 camera and projector lenses using a military standard for photographic lenses (MIL-STD-150) as a reference representing accepted definitions, nomenclature, practices and tests. This type of information is required to insure replacement lenses of high quality for photographic equipment.

MILITARY STANDARD-150 was published in October 1950 in order to fulfill the requirement for an authoritative document in which all necessary information concerning photographic lenses would be assembled from American Standards and other industrial and military sources. This 34-page document,¹ previously described by Kendall and Schmitt,² is the first of its kind to be issued by the Munitions Board Standards Agency since the unification of the Armed Services. It represents the effort of a large committee of engineers and scientists from industry, the military services, including the Signal Corps, and other Federal Agencies to combine into one document the basic definitions, test methods, and specifications needed to procure lenses suitable for many diversified applications. The Signal Corps has made extensive use of MIL-STD-150 as a reference document in specifications for equipment which employs photographic lenses.

High quality lenses are produced by American optical manufacturers and most of the cameras, projectors, and enlargers procured for military use come equipped with lenses designed to give good performance. Replacement lenses and certain other lenses procured for special purposes have presented difficulties since the government usually buys on a competitive basis and the quality requirements in the procurement information have often been of a rather nebulous nature.

A review of the procedures previously used by the Signal Corps for the procurement of photographic lenses will illustrate the problem. A camera, for example, is procured on a performance specification which defines the performance required of the entire camera, but usually does not prescribe design details. Replaceable parts of the camera are assigned stock numbers and stock number descriptions of 10 to 100 words which give information concerning the physical and mechanical features of the part and the manufacturer's part number but little information concerning quality.

Replacement lenses have usually been procured on an "or equal" basis using the short stock number descriptions. Results were often unsatisfactory. If awarded the contract, the manufacturer of the original equipment usually would supply satisfactory replacement lenses. In many instances, however, legal reasons require the contract to be awarded elsewhere, usually to the lowest bidder. Orders for replacement lenses were usually small and often no check was made of the quality of the product, especially since it is difficult to determine the quality of photographic lenses without extensive test

equipment. Furthermore, while the lens procured was required to be "or equal" to the original lens, exact information concerning the quality of the original lens was often not available. So the inspector had an impossible task, and consequently, replacement lenses procured for Signal Corps use were often of unsatisfactory quality.

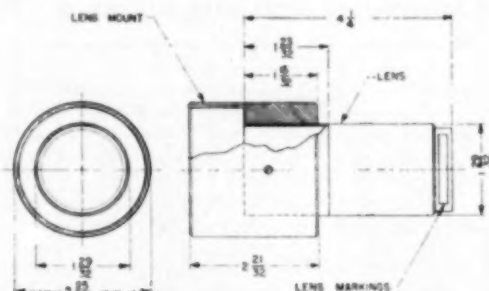


Fig. 1. Sketch of typical lens and mount used in Signal Corps SC-A drawings to indicate sufficient detail to insure that replacement lenses will be mechanically interchangeable with original equipment lenses.

Lens performance specifications have been prepared by the military services for many years. In general, these covered relatively few types of lenses which were procured in large quantities. A distinct need has always existed, however, for an authoritative document concerning the accepted tests, definitions, nomenclature, markings, and requirements of photographic lenses, previously scattered through various American Standards, industrial and professional literature, and military specifications. Military Standard-150 is the most complete document of its type available and its 34-pages are replete with authoritative lens information. Thirteen types of lenses procured for government use are listed and described. It lists and defines the terms which refer to the characteristics commonly associated with lenses. Specification tests for determining durability and lens quality are described and recommended. A reference list of 71 characteristics or requirements for lenses is given on pages 31 and 32.

Users of MIL-STD-150 should note that it is not a specification. To merely state that a lens shall be in accordance with the requirements of the standard is not enough. The military standard does not specify tolerance limits for such defects, as astigmatism, longitudinal chromatic aberration, lateral chromatic aberration, radial distortion, tangential distortion, spherical

* Signal Corps Engineering Laboratories, Fort Monmouth, New Jersey. Received 9 March 1953.

tances, apertures, resolving power, field curvature, color correction, distortion, aberrations, and flare. Lens performance under a severe range of environmental conditions is determined in the climatic test chambers where temperature and humidity conditions can be regulated over ranges encountered in military work from Arctic cold to desert heat or tropical humidity. A cathode tube shutter timer developed by the Signal Corps Engineering Laboratories records shutter performance and additional equipment for special tests such as flash synchronization is also employed where required.

The benefits of this program to the Signal Corps have been extensive. The detailed study of the stock lenses that are necessary to prepare the procurement documents brought out the fact that in many cases lenses which were functionally interchangeable had been stocked under two or more stock numbers because they were of a differ-

ent manufacture or installed in different equipment. In other cases it was determined that lenses were not required as there were suitable substitutes or the basic equipment was obsolete. As a result of this study 23 stock numbers for lenses were cancelled and the lenses are no longer procured. The program has also resulted in the procurement of lenses of uniformly high quality designed for use with the equipment on which they will be installed.

References

1. Munitions Board Standards Agency MIL-STD-150; "Photographic Lenses," October 23, 1950.
2. Kendall, C. W. and Schmitt, F. S.; "An Air Force Experience in Eliminating Guess Work," *Standardization*, Vol. 23, No. 7, July 1952, pp. 211-213 and 223.
3. Leistner, Karl and Marcus, Bernard; "Lens Testing Bench," *Journal of The Optical Society of America*, Vol. 43, No. 1, Jan. 1953, pp. 44-48.



HIGH-SENSITIVITY ELECTROPHORESIS-DIFFUSION INSTRUMENT

Based on a folded, figure-4 optical system, with an 18 inch optical path, the new Spenco* Model H Electrophoresis-Diffusion Instrument achieves double sensitivity by directing light through the cell and specimen twice. Other features include compactness and accessibility from the observation and recording position of operating controls and optical elements.

Optics are arranged to provide versatility in the observation and recording of boundaries by these five optical techniques: (1) Ordinary schlieren, (2) Cylindrical-lens schlieren, (3) Rayleigh interference fringes, (4) Gouy fringes, and (5) Mechanical scanning. The schlieren and Rayleigh patterns can be recorded simultaneously so that the rapid and accurate fringe-counting technique can be used in evaluating concentrations.

Isolation provisions have been made for the individual suspension and shock mounting of optical and controlled-temperature water-bath components to permit long undisturbed diffusion runs.

Housed in a single laboratory cabinet with dimensions 98 by 30 by 48 inches, the apparatus includes a servo-controlled cell turret capable of carrying three individual cell assemblies,

* Specialized Instruments Corp. 687 O'Neill Avenue, Belmont, California. Received 25 May 1953.

each of which is continuously connectable to an individually regulated and calibrated power supply. Any cell assembly can be rotated into position for observation or for automatic photography.

T. D. Technical Information Service

Dear Sir:

I am trying to make a split-image rangefinder, with a base of 6 inches or so: this to be combined with a vari-focal viewfinder. There is not much technical information available; at least I find very little. So I am writing the Technical Section of PSA for information. If you know of any references—text-books or scientific magazines, etc.—I would very much appreciate your letting me know.

I. C. Barker
San Francisco, Calif.

Dear Mr. Barker:

As Chairman of the Technical Information Committee of the Technical Division of PSA, I have the following to suggest on your request for information on Rangefinders.

The best general treatment is to be found in "Fundamentals of Optical Engineering" by Jacobs, published 1943, pages 249-281. This would cover the general theory but nothing about applications to cameras.

For specific applications to cameras I would suggest the current "1951 Edition of the Leica Manual" by Morgan and Lester as indicated in the index of that magazine.

Zeiss, Inc., New York City, might have something on the type that employs a rotating element rather than a movable prism.

Patent literature is probably the best place to find specific applications and details of the currently used types.

Public Libraries in Metropolitan areas usually contain brief descriptions of patents. You must first learn the classification under which rangefinders might be listed, and then search this classification. On finding something that seems applicable to the problem you have in mind, you can purchase a copy of the patent from Washington, D. C. I believe the price is 25c each.

Don Mohler, Chairman
T.D. Technical Information Committee
Nela Park, Cleveland, Ohio

PHOTOGRAPHIC SCIENCE AND TECHNIQUE

PHOTOGRAPHY IN OPHTHALMOLOGY

Dan M. Gordon, M.D.*

ADVANCES in the design and manufacture of diagnostic instruments in ophthalmology, coupled with modern photographic techniques, have made practically all parts of the human eye accessible to the prying inquiries of the photographer. The ophthalmologist who is camera conscious has an advantage over non-photographic minded confreres. In addition to advancing himself professionally by making use of photographic illustrations, he acquires a hobby of tremendous interest if he makes the photographs himself. In the writer's medical practice, photography has been helpful in four respects.

1. *In keeping records*, a permanent description of the patient's condition on a particular day is provided by a photograph. This is available to compare with later pictures to determine the progress or lack of progress the patient has made. In cases where the diagnosis is in doubt at the time the patient is first examined, the photograph provides a permanent record for later re-evaluation or for consultation with colleagues. On more than one occasion, the ability to study a photograph at some later date has led to a diagnosis which was impossible at the time of the patient's first examination. Instead of taking the patient, it is much easier to transport pictures to conventions or to doctors in distant cities and lands. In the case of a lawsuit, a photograph is the best possible record of the patient's condition at the time of the examination. It carries much more weight than any other part of the record.

2. *Illustrations for manuscripts* intended for publication in the ophthalmological journals are a valuable use of photographs. Lack in descriptive ability is often made up by excellent photographs.

3. *Teaching photographs* are indispensable in the instruction of undergraduate or postgraduate students. Here both still and motion picture photographs are invaluable. The man who uses photographs to enhance the vocal description, presents his case clearly to his audience and

captivates their interest. Further, since most people have strongly visual memories, pictures form a vehicle for a description which would be completely incomprehensible without illustration.

In medical teaching, pictures are of extreme importance in delineating the evolution of disease processes. One may start with the incipient disease and then show pictures of the lesion as it progresses to its final form or one may work backward with the disease, picturing it first in its final form and then showing how it reached that stage. Too often the physician or the ophthalmologist sees a disease process for the first time when it is in one of its end states. Unless he has observed similar disease processes evolving to that stage, he is at a loss to explain to himself or to the patient just how they got that way. However, if he has had the opportunity to watch similar diseases progress to that point, or has had the opportunity to study a series of pictures showing the progression of a disease, he is then completely clear on the subject.

Many pathological ophthalmic processes take a long time—often ten, twenty, thirty, forty or more years—to reach their end stages. It is impossible for any one physician in his life time to watch the complete evolution of certain clinical conditions because of the length of time involved. However, if one or more physicians take a series of pictures from the beginning to the end, then a very valuable set of photographs is available for the use of posterity. The author is now involved in the collection of just such a series of pictures of various night blinding diseases. Again, one may photograph various members of a family or different families with the same disease in different stages and by having available pictures of all of these individuals build up a set which can relate past and future heredity. The opportunities for the use of still and motion pictures in teaching are unlimited.

4. *Reporting*. This use of photography is, in a sense, part of the illustration use described under 2. However, this part may be called the "proof of the pudding." One may doubt our word but he cannot doubt unretouched pictures. Claims made for a new form of

*Cornell School of Medicine, New York, N. Y. Presented at the PSA National Convention, New York, N. Y., 12 August 1952 as part of the Technical Division Symposium on Photography in Medicine and Biology. Received 2 May 1953.

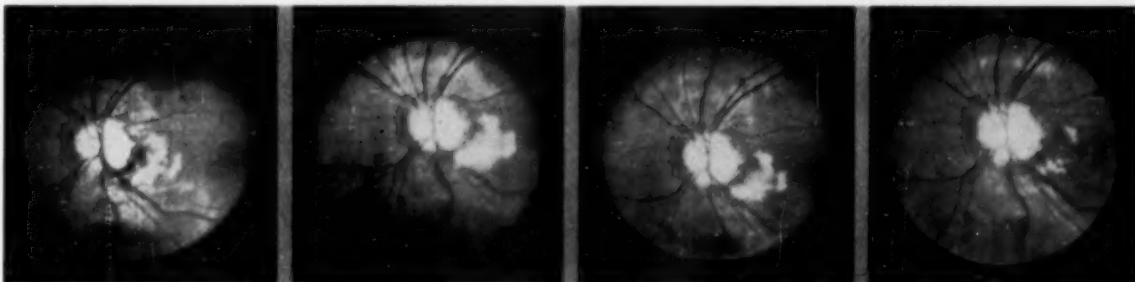


Fig. 1. Series of retinal photographs covering diagnosis and treatment of acute choroiditis. The pathology appears as an irregular white mass to the right of the disc of the optic nerve. The progression of the lesion after treatment with pregnenolone and its regression following administration of ACTH are clearly shown.

therapy may sound fantastic unless backed up by the irrefutable evidence of good pictures showing the disease before and after treatment.

One incident which very graphically illustrates this point occurred some years ago. A new and very dramatic type of treatment was introduced and was given the center of the stage at a symposium at a national meeting. Two of the more prominent speakers there had treated 16 and several hundred cases respectively with the new therapy. The first speaker, the man with 16 cases of experience, spent very little time in speaking but exhibited 16 excellent sets of before and after photographs showing the violent disease process attacking the eye and the then graphic evidence of the cure, following

treatment. When he sat down the audience "raised the roof." The second speaker, who had treated hundreds of cases spoke about his experience with the use of this new medication and presented graphs and charts but no color slides. When he sat down the applause was rather perfunctory. The audience which was dramatically stunned by 16 sets of excellent photographs was not sufficiently appreciative of a less graphic although much more extensive and important presentation.

While very few men can afford to own a fundus camera for taking pictures of the back of the eye, practically every ophthalmologist can afford to own some simple camera and lighting equipment for taking his own external eye pictures.

PURPOSES OF PHOTOGRAPHY IN THE GENERAL BIOLOGICAL SCIENCES

Wayne M. Hull, M.D.*

PHOTOGRAPHY has widespread application in biology. This is especially true in educational fields, where it is a facility of great importance. The value of visual aids has long been recognized in the lecture room and group study. In colleges, universities and elementary institutions throughout the country, instructors in the various sciences have built up teaching files of all kinds of biological photographs and are employing them daily. These pictures find frequent use in supplementing textbook study. Photographs are projected on the screen to serve as "life-like" models, permitting the instructor to point out and discuss fully the anatomy of the various systems, the physiological importance and relationship of organs, and the histological features that characterize them. In this way the student acquires a mental picture that is more lasting than the fruits of verbal memorization.

The applications of photography in the teaching of biology are not confined to the lecture room alone, for learning the subject is more important than learning the text-book. Pictures are used in some laboratories preceding anatomical dissection of biological specimens. Sequence pictures demonstrating the entire procedure are prepared, catalogued and filed for each subject and session in the laboratory. Thus before the student starts work he has a mental picture of the procedure, which provides more guidance than the usual laboratory manual and lecture notes alone. These pictures are not intended to replace the actual study, handling, and dissection of biological material, but to help orient the student and correlate his textbook and lecture instruction more quickly and with greater familiarity.

In advanced courses of instruction or graduate study, not only does photography supplement the lecture and text-book material, but more important, it makes available pictures of rare specimens which are otherwise un-

available for study. Photographs also provide an effective means for studying specimens difficult or impossible to obtain out of season. Pictures replace specimens too costly for general use or too large to bring into the laboratory.

Another important use of photography in biology is in the field of research where pictures are abundantly used to record the findings, under experimental conditions, of many investigative pursuits for later detailed study. Such analysis often reveals information not discovered or understood at the time of the original experiment. Photographs provide an undisputable record of changes and other scientific data the research worker needs. Finally, pictures are used extensively in publications to illustrate articles in journals and text-books, as well as for individual and group study in graduate schools.

A biological photograph should represent an accurate and faithful record of the specimen. It should show all essential detail clearly and sharply. To make pictures to satisfy the demands of the biologist, the photographer should first learn the intentions of the biologist; exactly what he wants to show in the picture. This will make the work less difficult, less likely of failure, and will certainly save the time of retakes. The specimen should be studied closely for the physical details since these characteristics will largely govern the equipment, magnification, type of film, accessories and illumination to be employed. The more information the photographer can gather about the subject the easier it will be for him to record it properly.

Field Work

Photography in the field is most often required for specimens which cannot be brought to the laboratory and for recording environmental conditions. Field pictures are in considerable demand for educational and research activities in botany, zoology and related branches of biology. Co-ordinated preparation on the part of both photographer and biologist is required. Planning ahead facilitates the work and shortens the time on loca-

* 104 South 39th Street, Omaha 3, Nebraska. Presented at the PSA National Convention, New York, N. Y., 12 August 1952 as part of the Technical Division Symposium on Photography in Medicine and Biology. Received 5 December 1952.

tion. The photographer should be thoroughly briefed on the type of specimen wanted, structural details desired and where it can be located. He will need to be prepared for close-up work as well as distant scenes in color and black-and-white.

Botanical specimens represent the most commonly photographed subjects in the field because drying subsequent to picking soon causes wilting of the leaves, loss of color, and drooping of the stems and branches. Whole plants lose their normal and natural appearance when laid flat on the table to be photographed and therefore are best recorded in an upright position. The photography of plants requires time, effort, and patience. A group photograph is commonly made with enough background to reveal the surrounding environment. Then a healthy, representative specimen free of defects is selected for the close-up views. It is often necessary to record special parts of plants such as catkins, pollen grains, blossoms, fruit and seeds, some of which can be taken to the laboratory provided drying effects cause no change. Two annoying problems interfere with the work—wind and shadows. The wind is the most disturbing and difficult to manage. The photographer may have to set up a wind break.

Animal Subjects

Biological specimens of animal species are usually brought to the laboratory, which is a more satisfactory procedure than working with them in the field. Many of these are water organisms of small dimension requiring the aid of high magnification equipment. Wild animals, birds, water and land fowl are most often photographed in the field with telephoto lenses, and present no particular problem other than getting the camera within suitable range.

Photomacrography and Photomicrography

In the biological sciences photomacrography and photomicrography probably constitute the most frequent application of photography. Most tiny specimens are available either in a living state, preserved in solutions, or in permanent mounts on glass slides. The photographer must be equipped to produce magnified pictures and for many of these very simple apparatus is sufficient.

Low power photomacrography is usually employed for specimens measuring 3 to 12 inches or larger using a camera with long extension bellows or extension tubes and short focal length lens. High power photomacrography (low power photomicrography) deals with specimens 3 mm to 3 inches; photomicrography deals with specimens less than 3 mm in size. Obviously some overlapping of these size ranges is permitted with the equipment ordinarily employed.

Equipment for low power photomacrography includes a rigid upright stand to support the camera in a vertical position and permit up and down movement, provision for ground glass focusing, long bellows extension (or a set of extension tubes) and a lens of shorter focal length than ordinarily used. Lighting will most often be a direct arrangement of two or more sources positioned for most effective rendition of the essential detail, and of course should be of the correct color temperature if color film is used.

Most specimens suitable for high power photomacrography (or low power photomicrography) are sufficiently transparent to be recorded by transmitted light, or a combination of transmitted and reflected light. Opaque or semi-opaque specimens generally require top lighting and some transmitted light to expose the background. Since these specimens require a magnification range between that for low power photomacrography and high power photomicrography a somewhat more elaborate set of equipment is needed. In the first place lenses of shorter focal length are required and in the second place a condenser system located behind the specimen stage is needed to concentrate the light on the specimen uniformly. Most optical goods manufacturers provide equipment especially adapted to this range of photography. Some utilize a large upright microscope stand with built-in illumination systems and equipped with special micro objectives and matching substage condensers. The micro objectives produced by the American Optical Company are listed as Micro-teleplats; those of the Bausch and Lomb Optical Company are listed as Micro-Tessars; those of Leitz are called Micro-Summars; and those of Zeiss, Microtars. Adapters to fit these objectives to standard lens mounts can be obtained. If much of this type of photography is encountered, a set of these special objectives is a worthwhile investment. The light source is preferably operated from an adjustable transformer or rheostat and when turned to full voltage should deliver an intense light of correct temperature for color film. A focusing condenser lens at the light source is desirable.

Specimens for high power photomicrography are nearly always supplied to the photographer in permanent mounts, usually glass slides with the specimen mounted in balsam. The procedure is analogous to that followed in photomicrography of histological and pathological slides as far as the manipulation of the microscope, substage condenser, and light source are concerned.

A great many of these specimens are stained by standard methods so no filters are required for color photography if the light source is capable of supplying a color temperature of 3200K. Filters may be required for different staining methods or for black-and-white photography, the colors of the dyes determining the filters to be used. Unstained specimens are recorded by the dark field or phase contrast technique.

The photography of small, living, water specimens is tedious and time consuming in preparation as well as recording. The rapid motion of these organisms darting in and out of the field makes it difficult to expose the picture at the right moment. If the camera is connected to the microscope by a micro adapter with beam splitter and side viewing telescope, the photographer can view the entire field continuously and make the exposure the moment the rapidly moving specimen enters the field. A shutter speed of at least 1/100 second and super-sensitive film are practical necessities.

Infrared Applications

The principal use of infrared photography in biology is to render certain structural detail of both plant and animal specimens that do not show with color film or panchromatic film. Infrared radiation has many applications in recording detail in thick micro specimens

or certain kinds of pigments and in penetrating the chitinous coating of insects and the dense cellulose material of plants. Infrared is of value in the study of plant diseases and helpful in the differentiation of various species of wood, some of which are transparent to infrared and some are not. Because of the inherent grain of infrared film, fine grain developer is recommended.

Fluorescence Photography

Many kinds of plant and animal tissues exhibit fluorescence under ultraviolet illumination. Various chemicals and drugs show this effect in animal and plant tissues. Two kinds of fluorescence effects are recognized: primary and secondary. Primary fluorescence refers to the natural or inherent characteristics of some tissues to show fluorescence without any special treatment. In the use of secondary fluorescence the specimen is treated with a fluorochrome (fluorescing dye) which is selectively absorbed. In biological research it is possible by this means to trace out the deposition and distribution of many substances in the living animal or plant structure. A good example of this application is in the field of nutritional research where certain vitamins, especially riboflavin and related compounds, show fluorescence in the tissues where they are stored or utilized.

Cleanliness is very important in the preparation of the specimen, fresh material being preferred, and the less treatment by fixatives, paraffin and other substances, the better the results. A strong light source such as the carbon arc is essential. A dark, ultraviolet-transmitting filter is introduced into the light path and special absorbing filters fitted into the microscope or over the camera. Viewing and focusing is carried out through a protecting filter to prevent ultraviolet burns of the eye. Exposures are usually long.

Photomicrography by Polarized Light

Polarized light can be used profitably to photograph many biological specimens. It is capable of rendering, in both plant and animal specimens, structural details which fail to show by any other method of reproduction. For microscopic work there are two essential parts (a) the polarizer, which may be of either calcite or polaroid sheet and is usually located just above the objective and (b) the analyzer, which may be a Nicol prism (also calcite) or a sheet polarizer. The polarizer usually remains stationary while the analyzer is rotatable. A rotatable stage is an advantage for rotating the specimen as viewed through the microscope after the light rays of the polarizing equipment have been crossed. Polarization studies can be made on practically anything that can be viewed through the microscope but not always with certain or definite advantages over other systems of illumination.

Phase Contrast System

The phase contrast microscope provides a most effective method of photographing living and transparent biological material. Biologists prefer the living fresh material whenever they can obtain it, as movement and other behavior provides much information not obtained in the lifeless and shrivelled stained specimen. The phase contrast system saves time since no special treatment is required and changes due to fixation, embedding and staining are avoided.

Dark Field Photomicrography

The dark field technique has its principal usefulness in the photography of very small specimens difficult or impossible to stain. Various strains of bacteria and molds reveal structural detail with dark field illumination that do not show under staining conditions. It is useful in recording distribution of pigments and sometimes the colloidal arrangement of proteins and other substances within the cell body. The main feature of the dark field microscope is the substage condenser; it is usually available for any standard type of medical or research microscope. The dark field condenser is so designed that a central stop interrupts direct rays of transmitted light from entering the field and focuses the peripheral rays of light onto the specimen, which is thus illuminated against a dark background. An oil immersion system is used for maximum resolution, but lower power objectives can also be used with some types of dark field equipment. A strong source of light is required for photographic purposes and polarizing and other types of filters can be used if needed.

The Electron Microscope

The electron microscope is an elaborate but valuable research tool capable of giving tremendous magnification compared to the optical microscope. The specimen is placed within the instrument in a high vacuum. Because of the poor penetrating ability of the electron stream as compared with ordinary light the specimen must of necessity be very thin. Photography is used extensively in conjunction with the electron microscope. The preparation of specimens suitable for the instrument requires considerable care, work, and time to render them suitable for study. Also, many of these specimens are not permanent so that photographs provide the only permanent trace of the original.

Microradiography and Autoradiography

These are relatively new techniques for gaining knowledge of fine biological structures. In the first, soft x-rays are employed to provide radiographic images on fine-grained Lippmann emulsions. This allows extreme enlargement of the detail—often 300 times. In the second, radioactive tracer elements, absorbed by the tissues, can be located by "contact printing" a section of tissue onto the photographic material.

Time Lapse Photography

The main purpose of time lapse photography is to make "visible" the many and various slowly changing features of living biological material under controlled conditions. It has great importance as a research and educational instrument in the study of living processes. The procedure is simply one of making large numbers of still pictures on motion picture film at relatively long intervals. When the film is run through a cine projector time is greatly condensed and the movement, growth multiplication, division and nutritional functions of specimens can be studied. Time-lapse photography has had extensive application in tissue culture work of both animal and plant life, and at present is widely used in cancer research, cytology and agricultural study of the

complete growth of plants from the germinating seeds to maturity.

The special equipment required for time lapse photography consists of microscope and phase equipment, 16mm camera, intense light source, time lapse exposure control unit, and prism beam splitter connecting microscope to camera. The control unit operates the camera

shutter, turns on the light for the exposure, then turns off the light and moves the film one frame for the next exposure. It is adjustable for exposure time and frequency.

It is hoped that this summarization shows the opportunities and importance of photography in biology. Certainly the uses are as numerous as the techniques are varied.

COLD-CATHODE LIGHT SOURCE POTENTIALS IN PHOTOGRAPHY

David B. Eisendrath, Jr., APSA*

ABSTRACT

The characteristics of cold-cathode light sources make them particularly applicable for photographic use. Factors which contribute to the increasing popularity of this illuminant are: accurate shaping of small diameter tubing to any design and length; control of color emission by variations of glass, gas, phosphor and selective filtering; constancy and evenness of illumination with continuous or intermittent use; and long life with minimum heat.

IN THE SHORT HISTORY of photography the illuminants used have usually been a matter of adaptation and compromise. Until the past few years particularly, it has been normal procedure to use available illuminants and to adapt the light to emulsion sensitivity thru use of filters, screens, reflectors, voltage regulators, etc.—or—to adjust emulsion response to the illuminant thru use of filtering, equipment or processing variants, or correction of developed image. Often available illuminants emit only a moderate percentage of photographically useful light. It has only been recently that manufacturers of lamps for photography have attempted to design and market illuminants efficiently matched to emulsion requirements. Of these, one of the most interesting from the point of rapid acceptance by photographers—more so, as a matter of fact than by some manufacturers of sensitized goods—is the cold-cathode light source.

Cold-cathode illuminants are by no means new—but their use in photography and their design and adaptation for photographic usage in recent years has been so marked and important that a discussion of their characteristics and potentials may be in order. Since few photographic technicians and even illumination specialists are aware of design characteristics, we need not apologize for a brief description of cold-cathode design and operation.

COLD-CATHODES: Basically a cold-cathode light is a low-pressure discharge lamp. It consists of a length of sealed glass tubing filled with a rare gas or gases at low pressure. Usually the inner walls of the tubing are coated with a fluorescent phosphor and often the outer walls are coated with a lacquer-plastic filter. Sealed into each end of the glass tubing is a cup-like shell of pure iron thru which the arc is struck. Except in rare conditions a small glob of metallic mercury is sealed into the tubing. When current of high voltage at low amperage is applied to the end terminals there is instant illumination from the passage of current thru the ionized

gas, and when used, from the fluorescence of the phosphors acted upon by the ultra-violet radiation within the lamp.

There are, however, many factors and variables which must be considered. Cold-cathode illuminants are instant starting. When first striking a cold-cathode light however, there is a slight increase in intensity as the tube reaches the temperature of greatest efficiency. In normal tubes this lies at a point somewhere between 110 F and 130 F. If the tube is maintained at this temperature, output is constant and unvarying; when constant intensity is required, preheating is customary and simple thermal controls and heaters maintain ambient temperatures. At operating temperatures lower than optimum, efficiency is not obtained; at temperatures higher than design requirements, phosphor efficiency and hence intensity is affected, as well as tube life. After initial heating, if optimum temperature is maintained, the lamp is constant, instant starting, considerably cooler in operation than incandescent sources, long lived, and extremely efficient—consuming very little current for useable illumination produced.

GLASS: The glass used may be soft or hard; Pyrex is sometimes employed. In practical usage tubing of 5mm to 25mm is employed, although sizes of 7mm to 15mm are most common. Tube size is chosen with consideration of greatest efficiency with regard to: power to be employed, length of tubing, gas pressure and desired shaping. In general smaller tubing has relatively greater resistance than larger tubing, and therefore greater intensity—but tube life and operation at optimum temperature are also governing factors. For most work clear glass is used, although tinted and colored glasses are often employed to obtain certain color emissions or to hold back unwanted wavelengths.

GAS: Gas pressure usually ranges between 4mm to 22mm of mercury pressure; as gas pressure increases, resistance increases. Pressure has no effect on either color or intensity but determines power necessary to strike the arc. Pressure also affects tube life, and high-

* Artisto Grid Lamp Products, Inc., 106-23 Metropolitan Ave. Forest Hills, L. I., New York. Presented at the PSA National Convention, New York, N. Y., 14 August 1952. Received 2 September 1952.

pressure tubes generally have longer life, though more power is required to operate them.

The gas, which acts as a conductor for the electric arc, is usually a selection and mixture of rare gases chosen because of intensity, color, and particularly to obtain optimum operating temperature with regard to tube size, power, and pressure. Gases most commonly used are argon, krypton, xenon, helium, and rarely, neon. Except where neon gas is used to produce red, small amounts of pure metallic mercury are used: its vapors creating the UV radiation necessary to activate the phosphors. It is interesting to note that the cold cathode illuminants with which we are most familiar in everyday life are those used in display signs. Originally neon gas was used in them—however with modern phosphors and increased knowledge, so called "neon signs" are seldom that. Incidentally, commercial display manufacturers are usually not equipped, skilled, or experienced in producing illuminants of value in photography.

It is also worthy of mention that not only design and housing of lamps is important in choosing and matching various factors affecting efficient operating temperatures, but in designing equipment for accurate work in northern climates or under unusual temperature conditions, gas mixtures may be chosen that will help to maintain satisfactory tube-wall temperature.

PHOSPHORS: Although there are hundreds of substances which emit light when activated by various means, there are in general a limited number used customarily with cold-cathodes. The silicates of zinc, cadmium, beryllium; the tungstates of calcium and magnesium; and certain organic phosphors are most commonly used. Generally activated by minute silver particles, finely ground, mixed, fired, and in other ways prepared, they are forced into clean glass tubes in an alcohol suspension, dried and baked under controlled conditions. Careful selection and mixing with regard to desired emission and other controlling factors permits a range of color and wave-length which allows any specified and desired transmission to be obtained. Although it is true that no single gaseous discharge tube has continuous line spectrum, a combination of tubes using selected glass, gas, phosphors, and selective filters can give effective transmissions equal to almost any other source, the range running from visible long-wave ultra-violet to near infra-red.

POWER: Normal operation of cold-cathode illuminants is at voltages of 750 V to 12,000 V a.c.; current employed is usually in the range of 30 milliamperes to 200 milliamperes. At higher amperages there is a slight color shift toward blue, and increased UV output may increase excitement of the phosphors. However, heat produced by increased amperage may create temperatures higher than optimum efficiency. At optimum temperatures there is maximum emission in the region of 2537 Å—it is to this wave-length that the phosphors react most strongly. Increased temperature produces greater internal pressure in the lamp and lines of strongest emission may then be at a higher point and from a region to which the phosphors do not so readily respond.

Higher voltage on the primary increases intensity up to the point of most efficient operating temperature and within efficiency range of transformers. The voltage on the secondary depends on resistance of the lamp: length, diameter, gas pressure of tube, and ambient temperature

affecting this. Although the light intensity of these lamps is affected by voltage irregularities they are not nearly so sensitive in this respect as incandescent sources; moderate voltage changes have no effect on emission characteristics—a decided advantage over other types of illuminants.

FILTERS: The external filters used on cold-cathodes in photographic use are coatings of lacquer-plastic formed permanently to the outer wall of the tube: they are tough, moisture-proof, heat-resistant. They may have color and transmission characteristics similar to almost any of the standard stable or near stable filters available for photographic purposes. Usually their function is that of selectivity or of cutting down excessive transmission of unwanted or overstrong wavelengths. Often, however, clear lacquer coats are used to give added strength or to help maintain efficient operating temperatures. Neutral density coatings may be used to balance tubes of different emission for similar photographic exposure.

ELECTRODES: Electrodes used today are pure iron shells attached to tungsten wires and sealed into tube terminals. The shells are coated internally with rare earth salts—such as barium—to produce maximum ionization of the gas in the lamp tube.

This is a unique light source: it can be made in continuous lengths, and it is not uncommon for industrial printers employing cold-cathode lamps to utilize 20 foot lengths in a section, the number of sections being unlimited. The lamps can be made in small sizes and often where small sources are employed, extraneous sections are opaqued off. They can be shaped to accommodate practically any requirement. Thru judicious selection of gas, glass, phosphors, and filtering material, almost any actinic effect may be achieved. They are cool, operating efficiency demanding temperatures of not more than 130 F at the lamp. They are long lived, average lamps give 5,000 to 10,000 hours of efficient service with a relatively low drop in intensity during useful life and no change in color emission. They are economical to operate, require moderate ventilation, and use a small fraction of the current consumed by incandescents for the equivalent useful, useable amount of light.

APPLICATIONS: There have been many attempts to design small compact lamp housings to be used for converting press-type cameras into enlargers. One major manufacturer has solved this problem expediently by means of cold-cathode illuminants. Not only is the unit compact and efficient, it is cool enough to afford no danger to camera, lens, or film.

Protection of film in enlargers has been an important consideration in press and commercial photography, particularly where many prints may be required and time demands are such that printing from wet negatives is practiced. Cold-cathode lamps adapted to standard enlargers not only satisfy these requirements, but provide more intense actinic light; meanwhile wet negatives are not jeopardized. These are in constant use by major newspaper services and newspapers. Note, incidentally, that the cold-cathodes are shaped and designed to be used on standard equipment: they are easily adaptable and do not require special enlarger design.

In order to obtain maximum printing efficiency on standard enlarging papers, some units were designed with lamps of a blue emission to which these papers are ex-

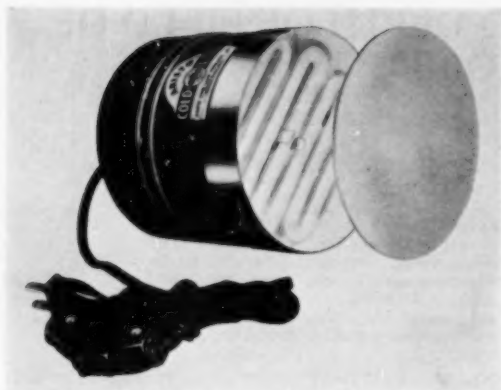


Fig. 1. Most common photographic application of cold-cathode lamps is in enlarger use. Here, cold-cathode grid and transformer are compactly housed in unit to easily interchange with condenser head on popular enlarger. Grid, held in place with friction clamps, can be changed for one of other color.

tremely sensitive. Photographers using them found that they were not effective on variable contrast papers when filters of green transmission were used. The lamps, being designed with strong blue emission had practically no green. It was easy to redesign a cold-cathode lamp which would give an equal balance of green and blue: selective filters could now be used with variable contrast papers and an even greater range of effective paper contrast was obtained than with the incandescent source for which the filters and paper had originally been designed. This lamp also operates efficiently with standard enlarging papers.

From here it was a jump forward to produce a novel and rather revolutionary device designed especially for printing American-made variable contrast paper without the use of filters, but highly efficient when used with standard projection material as well. This unit, designed and produced by Potter and Azan, provides a mechanical device for mixing the light of two enmeshed cold-cathode light sources carefully designed to match the blue and green response of American-made variable contrast emulsions. Similar devices are being used for contact printing as well. Because an unlimited number of mixtures of varying proportion of the green and blue are available here, more control is afforded and over a greater range than with filters of fixed transmission.

It is important to note the significance of an illuminant designed specifically to match accurately only the sensitivity of the emulsion. Further, the two enmeshed cathode tubes are designed and constructed to emit not only the precise spectral quality necessary for most efficient operation, but also to produce intensities so equated to emulsion response as to make exposure time equal with either tube or any mixture of light from both.

It was a natural step from a two light source mixing unit to a three source unit, using however, non-mechanical mixing devices. This unit contains light from red, blue, and green cold-cathode tubes. By limiting and controlling the intensities of each, an almost infinite

number of color combinations can be made. Experimentally, this device has already proven of great value as a background illuminator for microscopic photography where, instead of choosing filter combinations of gelatine and liquid to bring out or subdue stains and colors in specimens, a quick adjustment of the controls produces colors in controlled increments and any color combination can be repeated by resetting to the same position: in effect a variable Wratten-Rheinberg differential filter for backgrounds at the setting of a dial could be easily produced.

The same principle applied to transparency viewers has been used for making separation negatives, determining correction necessary for achieving desired color changes, correction necessary for reproduction, and serves as a rapid evaluator of filter effects. Applications of this unit are cropping up constantly for color matching, illuminating, experimenting, and evaluation.

Because shape and emission are so easily controllable, there are many applications in microscopy and medical photography. Ring lights for shadowless lighting are available in practically any size and color: in standard practice most popular lights are those approximating daylight, those satisfying requirements of color films designed for conventional photofloods or 3200K lamps, and long-wave ultra-violet. Since the illumination comes from one continuous source and not a series of small lamps, more uniformity and control is obtained.

For endoscopic photography it is not difficult to design small, cool illuminants that may be placed within the body cavity itself and will produce sufficient light of proper emission for color photography.

A unique application of cold-cathode lamps is in the field of reproduction materials. Kodak autapositive paper, film, and cloth is widely used for direct or reflex copying in normal room light. Highly blue-sensitive, the material is normally exposed thru a sheet of yellow or orange cellulose-ester material which transmits light of the proper color for exposing autapositive materials. Designed for use in moderate room light, autapositive materials are quite slow, normally being exposed on high-intensity printers containing arcs or photoflood lamps. Under some conditions the filter-sheeting sticks or may slip.

Here was an ideal challenge and opportunity to apply cold-cathode illuminants. The c-c autapositive printer is a simple contact printer, the lamp being a grid shaped tubing, with gases, phosphors, and selective filters chosen to give an intense emission in the region of the greatest sensitivity of the autapositive materials. This unit allows exposures in the neighborhood of ten to twelve seconds in duplicating letters by reflex or print-thru methods compared to exposures of two to three times as long with R2 photofloods. Here is an ideal example of cold-cathode economy: the lamp with a life expectancy of approximately 10,000 hours, takes less exposure time than 4 R2 photofloods in a standard high-intensity printer; the photofloods have a life expectancy of six hours. Not only does the grid give as much service as 1600 changes of bulbs (at a few dollars a change) but consumes about 1/4th the current. In addition, there is no heat problem, no depreciation of intensity or actinic quality, and a definite economy in space and weight.

THE DEPTH OF FOCUS AND DEPTH OF FIELD OF PHOTOGRAPHIC OBJECTIVES

John D. Hayes*

SUMMARY

Two of the most frequently confused and misused terms in photography today are *depth of focus* and *depth of field*. This paper attempts to set forth in a nontechnical manner the correct differentiation between the terms, and at the same time illustrate their interdependence. Graphical rather than mathematical means of illustration are used, though formulas representing more rigorous interpretation of the phenomena are included for the benefit of those who wish to make calculations of their own. The meaning of *circle of confusion* as it applies to both depth of focus and depth of field is illustrated and explained. The effects of lens aperture, focal length, subject distance, and image magnification are also reviewed.

THE LANGUAGE of photography today is filled with many technical and semi-technical terms, which, when passed along from photographer to photographer, acquire meanings only remotely related to their true concepts. Two of the terms, which have perhaps been confused and misused more than any others, are *depth of focus* and *depth of field*. These terms are not synonymous, as is believed by many. Furthermore, contrary to some popular conceptions there are no magical lens formulas that can be derived to increase either depth beyond those natural limits dictated by the laws of geometrical image formation, or to otherwise extend the limits judged acceptable by the viewer of the resultant photograph.

The most basic consideration in the determination of either the depth of focus or the depth of field of a lens is the selection of the limiting circle of confusion. No rigorous mathematical approach to this selection can be made, since the final analysis as to whether an elementary image (an "image point") is in or out of focus is a matter of personal judgment on the part of the observer. Experience has shown the choice of circles of confusion of diameters as given in Table I to be reasonable.

Table I

TYPICAL CIRCLE OF CONFUSION DIAMETERS FOR VARIOUS CAMERA SIZES

Camera Size	Diameter of Circle of Confusion
8 mm Motion Picture	0.0005 inches to 0.0010 inches
16 mm Motion Picture	0.0010 inches to 0.0020 inches
35 mm Motion Picture	0.0010 inches to 0.0020 inches
35 mm and Bantam Still Camera	0.0020 inches to 0.0030 inches

The depth of focus of a lens is dependent solely upon the size of the circle of confusion and the cone angle θ' of the image forming cone. The cone angle θ' is, however, a measure of speed, of the lens. This is shown mathematically as follows:

$$f/\text{-number} = \frac{\text{focal length}}{\text{Diameter}} = \frac{f}{2h} = \frac{1}{2 \sin \theta'}$$

Because of these geometrical relationships, any lenses of a common $f/\text{-number}$, will have the same depth of

focus if the same circle of confusion is assumed, regardless of the lens focal length, film coverage, object distance, or other parameters.

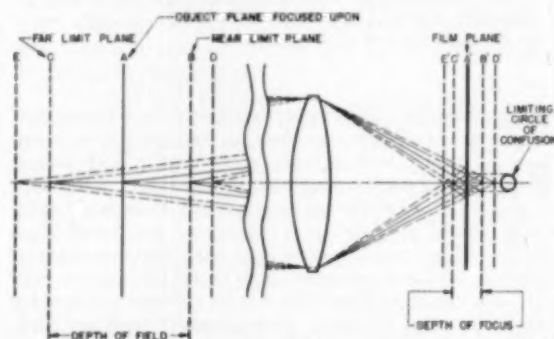


Fig. 1. Object Space—Image space relationship. The depth of focus $C'B'$ and depth of field C, B are conjugate image and object regions. The depth of field is the projection of the depth of focus region into the object space.

There are, therefore, only two changes that can be made to alter the depth of focus; either the speed of the lens ($f/\text{-number}$) is changed, thereby changing the angle θ' , or the size of the circle of confusion is changed. Either of these changes can be made to result in an increase or a decrease of the depth of focus.

A quick rule for determining the depth of focus of a lens may be obtained by assuming that the angle θ' is sufficiently small to permit the preceding equation to be written as:

$$\text{Depth of focus} = \frac{2y}{\sin \theta'} = 2 \times f/\text{-number} \times d$$

where $d = 2y = \text{diameter of the circle of confusion}$.

The depth of focus region is the image of the depth of field region. Knowing this relationship, we may determine the extent of a depth of field by using the data available in focusing tables, which list the displacements necessary to refocus a lens from one to another object distance.

Indeed, the geometry of Figure 1 may be interpreted to show that the far and the near depth of field limiting planes would come into exact focus on the film plane A' as the lens is shifted respectively toward or away from

* Scientific Bureau, Bausch & Lomb Optical Co., Rochester 2, New York. Presented at The PSA National Convention, New York, N. Y., 15 August 1952. Received 28 July 1952.

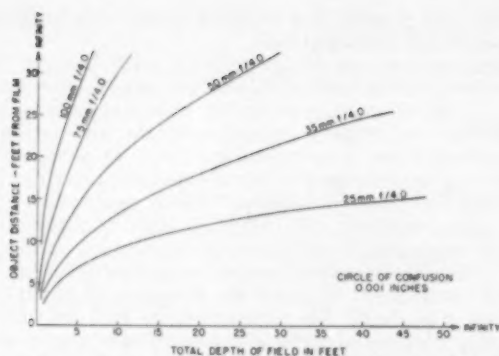


Fig. 2. Object Distance Versus Total Depth of Field. For any given object distance the total depth of field of lenses of different focal length is considerably different. For the same total depth of field the image magnification (reduction) produced by the lenses of different focal lengths is the same.

the film plane, the shifts being equal to one-half of the total depth of focus. Then, with the knowledge of the depth of focus under the given conditions, we also know the focusing shifts and can find the corresponding far and near limiting planes from a focusing table. Such a table was recently published by K. Pestrecov.¹

The effect of stopping the lens down is an increase in the depth of focus. Since the depth of focus indicates the maximum lens displacement permissible if the subject is to remain in focus upon the film, any increase in the depth of focus is associated with a greater permissible lens displacement.

The lens displacement required to refocus different lenses to a variety of object distances is roughly proportional to the square of the focal lengths of the lenses in question, a greater focusing shift is required to properly refocus the lens of longer focal length. This is characterized by a more shallow depth of field for the longer focal length lenses.

Figure 2 is a graphical representation of the total depth of field of various lenses showing that the depth of field greatly depends upon the lens focal length at all object distances, and that for any given object distance the lenses of shorter focal length always favored with an increased depth of field. It is noted, however, that when

the different lenses are focused so as to produce the same size image (to give the same degree of image reduction or magnification) the resulting total depth of field is the same. (This assumes the circle of confusion and f /number are the same.)

Many modern camera lenses have a depth of field scale as an integral part of the lens mount. This is particularly true of the high speed lenses and telephoto lenses, which have the most shallow depth of field. A typical scale is shown in Figure 3.

The use of this type of scale is simple and straightforward. The proper exposure is determined and the diaphragm actuating ring is set accordingly. The object distance is determined and the lens focused accordingly. Both of these settings are made to the common index. The intercepts of the f /number indicators of the depth of field scale with the focusing scale give the near and far limits of the depth of field.

This is the type of scale found on many of the motion picture and still camera lenses available today. Some cameras have depth of field indicators attached to the camera body. Most of the manufacturers instruction manuals include depth of field tables, and these tables may also be found in a number of the more popular handbooks on photography.

Reference

1. Pestrecov, K., A Theoretical Study of Errors of Focusing Scales. *PSAJ*, Phot. Sci. & Tech., Vol. 17B, No. 2, pp. 40 to 46 (April 1951).

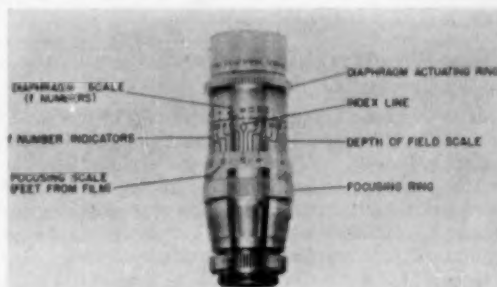


Fig. 3. Lens Mount with a Depth of Field Scale. Lens focused for an object distance of 10 feet, aperture $f/8$. Depth of field 8'7" to 11'11".

THE INTERNAL PHOTOGRAPHIC LATENT IMAGE

Photographic latent-image research has much in common with the workings of the law. In English law, a defendant is assumed to be innocent unless proved guilty. This proof constitutes the main difficulty when the evidence is all circumstantial, and it is here that the similarity lies. In photographic research, the latent image is destroyed during development and, in fact, no evidence can be obtained except by a procedure which involves development. All evidence on the latent image is therefore circumstantial. Internal latent image is by definition a change in the interior of the grain which causes the grain to be developed only if the grain surface has been or is being removed. Latent image which develops in the absence of grain

Received 24 April 1953 from G. I. P. LEVENSON for the Scientific and Technical Group of The Royal Photographic Society.

solvents is termed superficial. These two kinds of latent image have widely different properties and the distinction between them has proved to be very valuable in photographic research, accounting for and correlating a large number of photographic effects.

These were the introductory remarks to a lecture by Dr. G. W. W. Stevens to the Scientific and Technical Group of the Royal Photographic Society on 16th April. His report gave valuable additional evidence on the existence of latent image nuclei which, from their behaviour, have to be assumed to be situated well inside the grains. His technique was based on two important refinements; the use of single layer plates so that all grains could be assumed to have received the same treatment and the method of assaying both silver halide and

silver by means of radioactive iodine applied as the iodide. This highly sensitive method allowed very small amounts of material to be assessed with certainty.

Dr. Stevens proved that in order to reveal the internal latent image by the "internal developer" most commonly used, an amount of silver halide had to be removed from the grains which was sensibly constant regardless of the silver halide solvent employed. The depth of this internal image is of the order of 20 ion pairs below the grain surface. This was on the assumption that the solvent attacked the grain evenly; the depth would be greater if the solvent action were uneven and specially strong near the latent image nucleus. By partly dissolving the grain in stages, bleaching any silver which may be present on the grain surface and then developing for the remaining internal latent image, he was able to show that internal image occurs right through the depth of the grain, the effective sensitivity of the internal image formation dropping appreciably only when the major portion of the total silver halide had been dissolved away. This contradicts statements made in the literature, according to which a deep internal latent image is formed only for much heavier exposures than are necessary to produce the normal internal latent image which is situated just underneath the grain surface.

The lecture and the subsequent discussion left no one in doubt that the culprit, the internal latent image, was indeed often present at the scene of the crime and that its function in photography was as real and plausible as has been made out in earlier papers on this subject.

New Photographic Standards Committee

A new Sectional Committee operating in the field of photography was organized by the American Standards Association June 25, 1953 to deal with national standards for photographic documentation. Requests for the development of American Standards in this field had come to the ASA from library organizations, from office equipment and microfilm apparatus manufacturers.

The need for a new committee to deal with photographic documentation problems was established at a General Conference called by the ASA in New York City on May 21, 1953 to which some 50 or 60 organizations of national importance were invited. This general conference, under the Chairmanship of Paul Arnold, APSA, Chairman of the ASA Photographic Standards Board, recommended the establishment of a new sectional committee under the sponsorship of the Council of National Library Associations.

The new Sectional Committee PH5 on Photographic Documentation will assume jurisdiction over existing American Standards in that field.

The organization of Sectional Committee PH5 provides the American Standards Association with a means for effectively participating in international standards activity. Under the secretariat of the French national standards body, work on international standards for microfilm has been under discussion during the past two years in ISO Technical Committee 46 on Documentation which has set up a Subcommittee No. 1 on Photographic Documentation. An international meeting of the Subcommittee was held in Paris July 1 to 4, 1953 to further

explore the possibilities of international standards for photographic documentation.

International standards activity with respect to photographic documentation has four aspects at present: (1) a study of existing microfilm readers stimulated by UNESCO who made a contract with the International Organization for Standardization (ISO) as a basis for achieving uniformity of national standards covering the characteristics and performance of such equipment. (2) ISO recommendations for standard sizes of paper used for photographic reproduction of documents that are readable without optical devices. (3) Establishment of an ISO test object to check the sharpness of document images reproduced by photography. (4) An international glossary of terms applying to microcopies and their definitions.

C. LOCHER

THE CHARACTERISTIC CURVES OF THE HUMAN EYE

The Weber-Fechner Law concerning the response of the eye to changes in brightness in the subject states that, over a considerable range, sensation magnitude is proportional to the logarithm of the luminance, I , of the stimulus.

The Weber-Fechner law accords with general experience inasmuch as increasing the amount of light falling on a photographic print, or viewing a scene through a neutral filter, does not alter the apparent contrast. Although the law has been the object of much criticism, it continues to flourish. According to Dr. R. W. G. Hunt, this is perhaps because nothing has been suggested to take its place. Its great value is that it does provide characteristic curves for the eye; its chief weakness is its baseless assumption that the discrimination step ΔI always corresponds to the same sensation difference.

Presenting a paper on "The Characteristic Curves of the Human Eye" before the Scientific and Technical Group of the Royal Photographic Society on May 14th, Dr. Hunt described an attempt to derive for the eye, under various states of adaptation, curves which do not suffer from the inherent weakness of the Weber-Fechner law. This Dr. Hunt did by assuming that the size of the discrimination step ΔI depends upon physiological, and not psychological, factors. He assumed that when a stimulus is viewed, the magnitude of the physiological response is a function of the intensity and the concentration of the photochemical substance involved.

The core of the discussion is the assumption that the apparent brightness is determined by the number of nerve impulses, that the number of these depends on the rate of absorption of light, and that the last is controlled by the amount of photosensitive material involved. The amount of photosensitive material is controlled by the light intensity because it is easily bleached. The equation which Dr. Hunt obtains thus contains essentially two variables, one of which—the nerve impulses—is equivalent to apparent brightness—and the other—the concentration of photochemical substance—is equivalent to the adaptation.

The curves obtained in this way are consistent both with apparent brightness and contrast data, and with electrophysiological studies, and they permit a simple quantitative explanation of the variation of luminance discrimination with field size.

Received 26 May 1953 from G. I. P. LEVENSON on behalf of the Scientific and Technical Group of The Royal Photographic Society of Great Britain.

Properties of Developing Agents.

III. Combinations of Aminophenols and Hydroquinones*

R. W. Henn

SUMMARY

Nine paraminophenols were tested in combination with hydroquinone, and in some cases, with chlorhydroquinone, at several pH levels. The properties of the mixtures, including both photographic activity and rate of aerial oxidation, were determined largely by the aminophenol rather than the hydroquinone. The slope of the density : log-time curve (time-rate function) was also that of the aminophenol. The combinations showed advantages over the separate agents in improved activity and selectivity.

THE FIRST PAPER of this series¹ described the developing properties of a group of hydroquinones, the second,² the properties of a group of paraminophenols. This paper concerns combinations of the two types of developing agents—hydroquinones and paraminophenols. The conditions of these experiments were the same as those described in the first paper, and employed Kodak Fine Grain Positive Film developed with high agitation for a wide range of times.

The basic developer formula contained:

A paraminophenol* and/or	0.02 mole per liter
A hydroquinone**	0.02 mole per liter
Sodium sulfite	0.20 mole per liter
Buffer	0.10 mole per liter
Sodium hydroxide	As necessary to obtain pH

* The paraminophenols employed included:

No.	Name	Group
I	Paraminophenol (unsubstituted)	A
II	N-Methyl <i>p</i> -aminophenol (Elon***)	A
III	N- β -Hydroxyethyl <i>p</i> -aminophenol	A
IV	N- β -Aminoethyl <i>p</i> -aminophenol	A
V	N-Sulfomethyl <i>p</i> -aminophenol	B
VI	<i>p</i> -Hydroxyphenylglycin	B
VII	N-Methyl- <i>p</i> -hydroxyphenylglycin	B
VIII	N-Methyl-2 (or 3)-chloro-4-aminophenol	A
IX	N-Methyl-2 (or 3)-sulfo-4-aminophenol	B

** The hydroquinones examined in combination with these aminophenols included:

X	Hydroquinone (unsubstituted)
XI	Chlorhydroquinone

*** Trademark of Eastman Kodak Company

The formulas of these compounds are given in the earlier papers in this series.

Certain terms, which have been employed in preceding papers, will be defined here to aid in the presentation of the experimental results. Much of this interpretation is based on the linearity of the density : log-time plot, as shown, for example, in Figures 1 to 5. The slope of this curve, which may be called, as explained later, the "time-rate" function, becomes an important characterizing quantity. The slope is also used, in a less strict sense, as an indication of developing rate.

The induction period has been obtained by continuing the straight-line portion of the density : log-time plot to

zero density and is slightly greater than if measured by the actual appearance of the first traces of the image. The activity of the developer is a function of both of these quantities—that is, the time for the image to appear and the subsequent rate of growth. The degree of development selected as the criterion has been that at which the density of the fourth step equals 2.0 and corresponds well to the degree of development employed with this material in practice.

Aeration life, as used here, is obtained from a plot of the image density obtained for a fixed developing time against the time of aeration in an open flask. The value taken is that at which the activity of the developer has decreased to such an extent that only one-half the original density is obtained. Aeration life has also been measured in terms of discoloration. In this case, the light (wavelength, 450 m μ) transmitted by a 1-cm sample is plotted against the aeration time and the value taken is the time when this falls to one-half the light transmitted by the original sample.

Experimental Results

The various combinations of hydroquinone (X) and chlorhydroquinone (XI) with methyl *p*-aminophenol (II) and hydroxyethyl *p*-aminophenol (III) were studied in some detail over the pH range of 8.5 to 12.8. These combinations included:

1. Methyl *p*-aminophenol + hydroquinone
2. Methyl *p*-aminophenol + chlorhydroquinone
3. Hydroxyethyl *p*-aminophenol + hydroquinone
4. Hydroxyethyl *p*-aminophenol + chlorhydroquinone

The data obtained are presented in Figures 1, 2, 6, and 7 and in Table I. Figure 1, which represents a plot of the fourth step density against the logarithm of the developing time at various pH levels, applies to combination 1, methyl *p*-aminophenol and hydroquinone. Hydroquinone is seen to be developing only faintly at a pH of 8.5, while methyl *p*-aminophenol develops quite vigorously. The addition of the hydroquinone to methyl *p*-aminophenol, while it does little to shorten the induction period, markedly accelerates the developing rate and produces an increment of about 20% in density for a given time of development.

At the higher pH levels of Fig. 1b, 1c, and 1d, the activity of both methyl *p*-aminophenol and the hydroquinone is increased. The increased activity of the methyl *p*-aminophenol is evidenced in both an increase

* Communication No. 1529 from the Research Laboratories, Eastman Kodak Company, Rochester 4, New York. Received 12 January 1953. Part I. Hydroquinones appeared in the July 1952 issue. Part II. Paraminophenols appeared in October 1952.

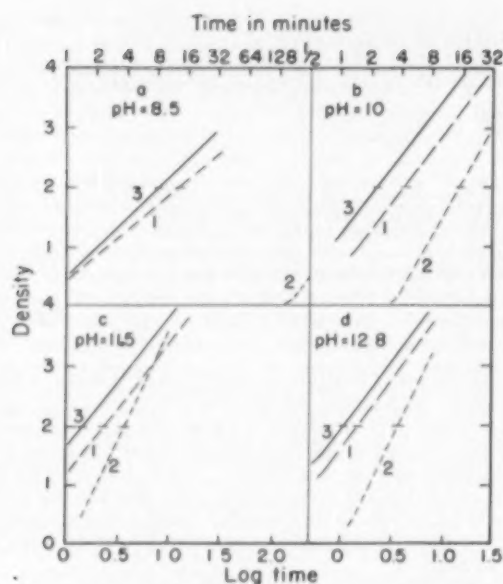


Fig. 1. Density:log-time curves for (1) methyl *p*-aminophenol, (2) hydroquinone, and (3) the combination, at various pH levels.

in rate (or slope) and a reduction of the induction period, while the increased activity of the hydroquinone is marked by a large reduction in induction period which has changed from 2 hours at pH = 8.5 to 3.5 minutes at pH = 10.0. In every case, the activity of the combination of agents is greater than that of either alone. Thus, while the rate parallels that of the methyl *p*-aminophenol, the induction period is reduced, to produce a decrease of 20 to 40% in time for a given density or a density increase of from 0.25 to 0.5 units for a fixed time.

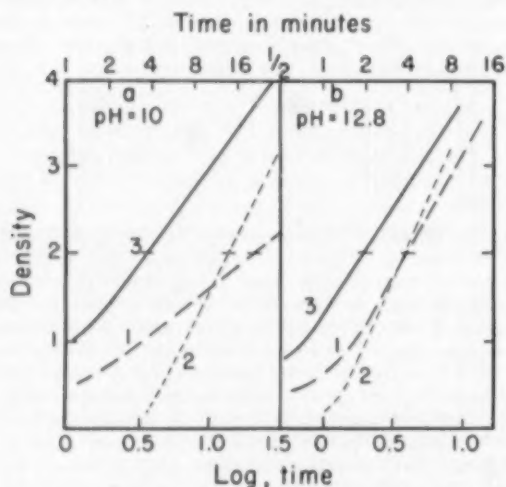


Fig. 3. Density:log-time curves for (1) methyl-chloroaminophenol (agent VIII), (2) hydroquinone, and (3) the combination at pH = 10 and at pH = 12.8. Note the strong reinforcing effect and marked acceleration of development.

Next, let us consider combination 4, where the other two agents were employed. In Figure 2a, the chlorhydroquinone may be seen to have an appreciable activity at a pH of 8.5, while the activity of the hydroxyethyl-*p*-aminophenol is slightly less than that of the methyl *p*-aminophenol of Figure 1. The addition of the relatively active chlorhydroquinone exerts a marked influence on the slope of the aminophenol, increasing density by about 45%, but again not appreciably affecting the induction period. At the higher pH values (Fig. 2b, 2c, 2d), the effect is, as with methyl *p*-aminophenol and hydroquinone, a translation of the aminophenol curve amounting to a 20 to 35% decrease in developing time.

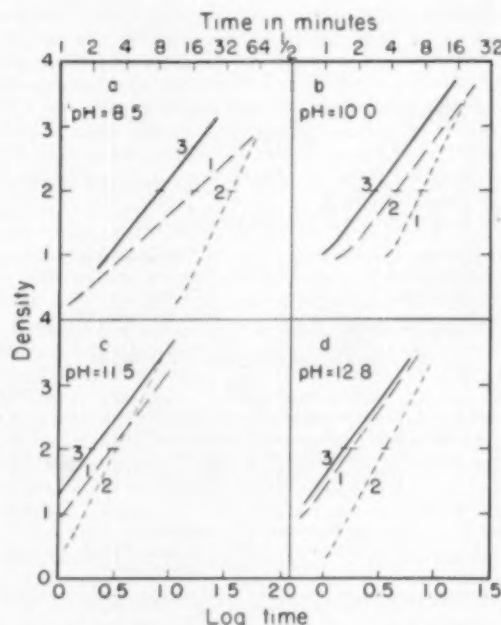


Fig. 2. Density:log-time curves for (1) β -hydroxyethyl-*p*-aminophenol, (2) chlorhydroquinone, and (3) the combination, at various pH levels.

It has not been felt worthwhile to present in detail the results obtained with combinations 2 and 3. Combination 2, in which the chlorhydroquinone was combined with the methyl *p*-aminophenol, is similar to combination 4, modified by the slightly higher activity of methyl *p*-aminophenol. Thus, at a pH of 8.5, the increase in density for a fixed time amounted to 30%, whereas the decrease in time for a fixed density amounted to 20 to 30%.

In these combinations, the aminophenols had considerably higher activity than the hydroquinone, and the increased activity produced by the addition of the hydroquinone was only moderate. The relative influence of the hydroquinone becomes more important when the activity of the aminophenol (used alone) is not high. In Figure 3, the chlorinated aminophenol, VIII, has been employed. The activity of this agent is roughly comparable to that of hydroquinone, although its rate

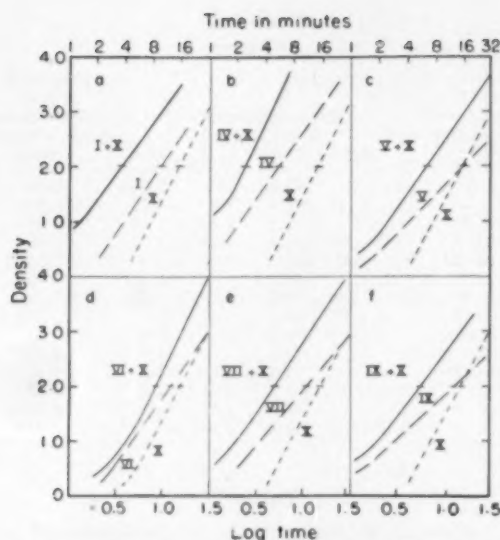


Fig. 4. Density:log-time curves for various aminophenols, hydroquinone, and combinations at pH = 10.0. The agents are numbered as in the introductory section of this paper.

(slope) is less. The combination is seen, at a pH of 10, to produce nearly twice the density given by the aminophenol alone (that is, to have double the time-rate function), while at a pH of 12.8, the addition of the hydroquinone has cut the induction period and the developing time by 60%.

The results obtained with combinations of the other aminophenols with hydroquinone are shown in Figure 4 for a pH of 10.0, and in Figure 5, for a pH of 12.8 (caustic solution). The same two effects are observed in the earlier figures, (a) an increase in rate (slope) with little effect on induction period, or (b) a decreased induction period with little effect on rate. The activity figures

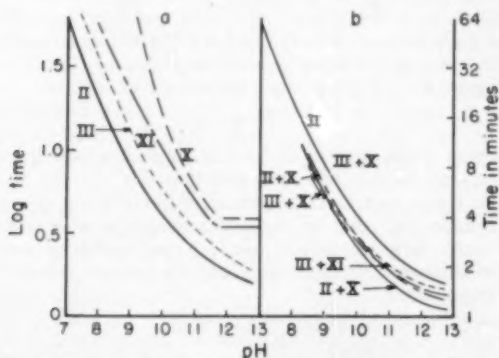


Fig. 6. The change of developing activity with pH. Figure (a) applies to separate aminophenols and hydroquinones, Figure (b) to combinations. Methyl *p*-aminophenol (II), used alone, is included for comparison. The pH response curves of the mixtures are closely bunched, and they are reasonably parallel to curve II.

are also given in Table I, where they are compared with methyl *p*-aminophenol (II). It will be seen that the activity of the combinations varies from about 45% to 165% that of the methyl *p*-aminophenol-hydroquinone developer at the same pH. This is a range of about 1:3, whereas the activity of the separate agents varied by a factor of about six times.²

Fog. The selectivity of the aminophenol-hydroquinone combinations proved good, and was generally better than that of hydroquinone. These fog values, as obtained for forced development ($D_1 = 3.0$) are listed in Table II. In general, the less active agents gave the least fog, but there were some exceptions. Agent IV, aminoethyl *p*-aminophenol, which fogged very badly alone, produced much less fog when combined with the hydroquinone, although it was still high. (For example, when developing at a pH of 10.0 and a total den-

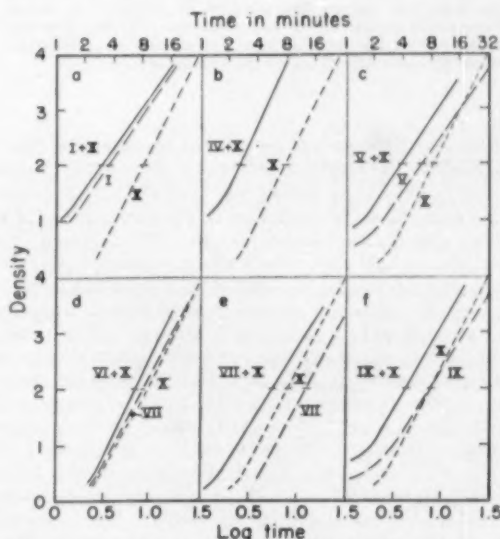


Fig. 5. Density:log-time curves for various aminophenols, hydroquinone, and combinations at pH = 12.8.

sity of 3.0, agent IV produced a fog of 1.8, whereas in combination with hydroquinone, this was reduced to 0.65.)

Activity as a Function of pH. In Figure 6a are plotted the activity of methyl *p*-aminophenol (II), hydroxyethylaminophenol (III), hydroquinone (X), and chlorhydroquinone (XI) against changes in pH, while Figure 6b shows the response of combinations of these agents. Note that whereas the difference in activity of the several agents employed separately is great (e.g., covering a range of 3.8 to 14 minutes at a pH of 10), the difference between the combinations is slight, varying only between 2.3 and 3.0 minutes at the same pH. Also, the shapes of the various pH-activity curves are, allowing for some divergence at the extremes, very similar and characteristic of the aminophenols rather than of the hydroquinones.

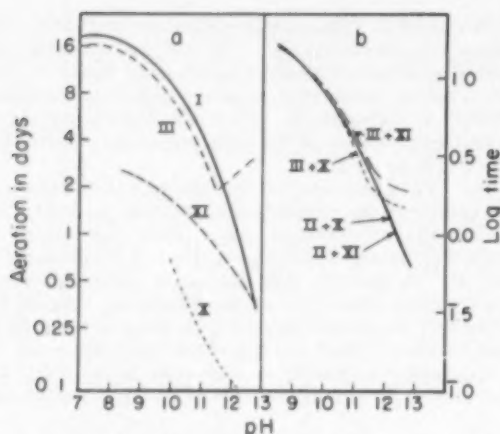


Fig. 7. Aeration curves. The half-activity lives of the separate agents are plotted in Figure (a), while Figure (b) applies to the combinations. Note again the wide separation of the separate agents as compared with the close bunching of the combinations.

Aeration. In Figure 7 are plotted the aeration life, as measured by the loss in activity (see above), against the pH for (a) the separate agents, and (b) combinations. Note again the wide differences in the aeration life of the several agents, the hydroquinone (X) aerating little more than a half day, while the paraminophenol solutions aerated for eight days before falling to half-activity. The unique resistance of the hydroxyethyl compound (III) at high pH is also clearly shown. Nearly all of these differences, however, have disappeared when the agents are combined (Fig. 7b), and the aeration lives in most of the pH range are so close as to be almost interchangeable and are substantially those of the *p*-aminophenols. Similarly, the aeration lives of agents I, IV, V, VI, VII, VIII, and IX, when combined with hydroquinone, were very close to those of several aminophenols aerated in the absence of hydroquinone. Also, discoloration of the solutions was quite parallel with loss of activity, a property previously found characteristic of aminophenols but not of hydroquinones.

Discussion

The data of this paper were gathered primarily to compare the properties of variously substituted aminophenols and hydroquinones but they also offer some contribution to the understanding of dual developing agent systems. This is due not only to the large number of developing agents examined, but also to the wide ranges of time and pH considered. Furthermore, the choice of a density-log time plot has been particularly helpful in characterizing the agents. The slope of this plot gives a value which is not only (unlike "rate") independent of the value of time and density selected, but is often identical over wide pH ranges and among different agents of the same ionic type.

1. **The Density-Log-Time Curve.** It is common practice to plot density as a function of time, and such a curve, for data obtained with hydroquinone at a pH of 11.5, is shown in Figure 8a. The developing rate, r , as usually

Table I

ACTIVITY

Developing Agents	Time in Minutes for $D = 2.0$ at pH of				Relative to Methyl <i>p</i> -Aminophenol + Hydroquinone (Average)
	8.5	10.0	11.5	12.8	
I + X	...	3.4	...	1.5	0.73
II + X	8.5	2.3	1.4	1.15	1.00
II + XI	7.5	2.3	1.8	1.30	0.96
III + X	9.0	2.8	1.85	1.30	0.81
III + XI	8.0	2.8	2.0	1.5	0.83
IV + X	...	2.5	...	1.3	0.90
V + X	...	6.2	...	2.0	0.48
VI + X	...	8.2	...	3.2	0.34
VII + X	...	5.1	...	2.8	0.43
VIII + X	...	3.5	...	2.0	0.62
IX + X	...	5.5	...	2.0	0.50
X	13.0	2.8	2.3	1.4	0.68
XI	...	14.0	4.0	4.0	0.23
XI	...	10.0	3.5	3.5	0.32

Table II

FOGGING PROPENSITY—FORCED DEVELOPMENT ($D_i = 3.0$)

Developing Agent	Fog at pH =	
	10.0	12.8
I + X	0.17	0.25
II	...	0.25
II + X	0.13	0.24
II + XI	0.16	0.20
III	0.12	0.18
III + X	0.12	0.17
III + XI	0.12	0.18
IV + X	0.65	1.25
V + X	0.21	0.31
VI + X	0.22	0.52
VII + X	0.17	0.30
VIII + X	0.16	0.33
IX + X	0.15	0.21
X	0.20	0.5
XI	0.15	0.2

defined, is the slope of the curve at some arbitrary value of density, D , and time, t . Expressed differentially,

$$r = dD/dt. \quad (1)$$

In these papers, density has been plotted as a function of log time, and a linear relationship obtained, as shown in Figure 8b. The equation for this line is

$$D = m \log t/t_0, \quad (2)$$

where m is the slope and t_0 is the time of appearance of the image, or the induction period.

The rate, r , is a variable, which shifts (e.g., r_1, r_2) with each value of time or density selected as a criterion. However, m is a constant. It is a time-rate function; it is r made independent of time, and the two are related by the expressions:

$$r = m/t, \quad \text{or} \quad m = rt. \quad (3)$$

Since we have given m in terms of base ten logarithms, these expressions, to be arithmetically correct, should be:

$$r = m/2.3t, \quad \text{or} \quad m = 2.3rt. \quad (3a)$$

2. **The Dominating Nature of the Aminophenol.** A study of the data obtained with the combinations of agents, as

Table III

Developing Agent	RATE-TIME PRODUCT			
	Slope ($D/1.0 \log t$) at pH =			
	8.5	10.0	11.5	12.8
I	1.32	2.56	2.6	2.6
I + X	...	2.41	...	2.5
II	1.34	2.44	2.40	2.47
II + X	1.65	2.40	2.35	2.47
II + XI	1.80	2.42	2.44	2.42
III	1.40	2.44	2.5	2.45
III + X	2.14	2.45	2.45	2.45
III + XI	2.14	2.40	2.44	2.40
IV	1.09	2.52
IV + X	...	3.6	...	3.6
V	...	1.81	...	2.50
V + X	...	2.44	...	2.50
VI	...	2.44	...	3.35
VI + X	...	3.3	...	3.46
VII	2.5	2.45	2.55	3.1
VII + X	...	2.54	...	2.9
VIII	0.78	1.28	1.97	2.7
VIII + X	...	2.31	...	2.48
IX	1.65	1.64	2.25	2.27
IX + X	...	2.31	...	3.14
X	...	3.3	3.3	3.3
XI	3.3	3.3	3.3	3.3

compared with those obtained with the individual agents, discloses to how great an extent the aminophenol influences the properties of the mixture. It is the aminophenol that determines the developing rate—or at least the time-rate function, the pH response, the fogging characteristics, and the rate and nature of the aerial oxidation. The contribution of the hydroquinone is to (1) modify the rate within the time-rate limits characteristic of the aminophenol, or (2) reduce the induction period, and (3) possibly improve the selectivity.

Perhaps the slope of the D -log t curve (the time-rate function) shows these influences the most clearly. Thus, the slope, m , of the time-rate function of group A of the aminophenols (I, II, III, IV, and VIII) is characteristically about 1.3 density units per log t at low pH values and 2.5 at pH values of 10.0 and above, corresponding presumably to (a) the un-ionized, and (b) the singly ionized molecule. The addition of hydroquinone or chlorhydroquinone tends first to increase this rate to the higher value (Fig. 1a, and 2a). Then, secondly, if this rate has been obtained, it tends to shift the curve to the left, decreasing the induction period, but maintaining the slope value of 2.5 (compared with the value of 3.3 characteristic of hydroquinones). In the case of the group B aminophenols, which have charged groups in the molecule, the addition of the hydroquinone may also increase the slope, but in this case from 2.5 to 3.3, which is the value of the doubly charged ion. (Note the combination of glycine (VI) and hydroquinone, Table III. However, the slope of 3.3 is given by glycine alone at pH values over 11.5.)³

The aminophenol tends to control the developing reaction even if present in small proportions. Data obtained from a mixture of 0.02 molar hydroquinone combined with 0.002 molar methyl *p*-aminophenol at a pH of 10.0 are plotted in Figure 9. Curve *a* is for the combination of agents, Curve *b* for 0.02 molar hydroquinone. Note the characteristic methyl *p*-aminophenol slope (approximately 2.4) and short induction period of Curve

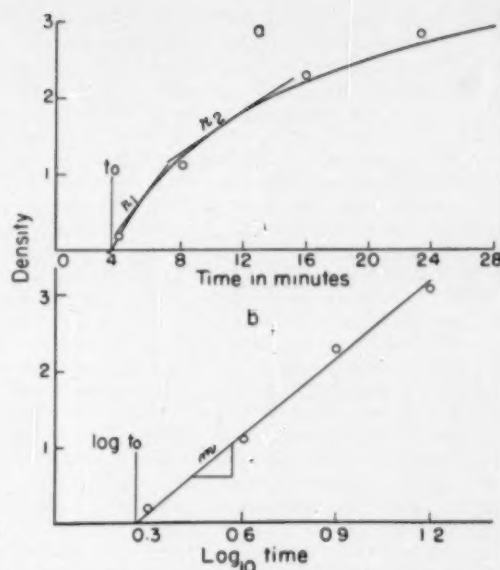


Fig. 8. A comparison of (a) a density-time plot with (b) a density-log-time plot. The developing rate is a variable, r_1 , r_2 , etc., according to the point at which it is taken. The time-rate function, m , is constant, however. The time of the appearance of the image is represented by t_0 .

a. In addition to dominating the developing reaction, the methyl *p*-aminophenol also controlled the fogging and aeration reactions. Thus, fog values were little more than one-half those obtained with the hydroquinone at equal degrees of development, while the combination had a half-activity life of 2.5 days as compared with less than 1 day for the hydroquinone alone.

3. **Additivity and Superadditivity.** The practical value of combinations of methyl *p*-aminophenol (Elon) and hydroquinone lies in obtaining, by the combination, properties not obtained with the separate agents. One of these properties is a greater degree of development than would be expected by merely adding the development produced by the methyl *p*-aminophenol to that produced by the hydroquinone. This "superadditivity" has been studied for methyl *p*-aminophenol and hydroquinone and for other combinations of agents by a number of investigators.^{3,4,5,6} The criteria selected for expressing the degree of development include (a) density in a given time, (b) rate (dD/dt) at a given time, or (c) rate at a given density.

Figures 1-5 disclose many cases of superadditivity, particularly in the short times of development, while in the long times the degree of development is often less than additive. This variation is due to the high rate-time function of hydroquinone (and chlorhydroquinone), that is, to its vigorous progress of development, once initiated.

In the extreme case of Figure 1a, where the induction period of the hydroquinone is of the order of 2 hours, any increase in rate of the combination is "superadditivity." However, in Figure 1c, where the induction period of hydroquinone is about 1 minute, the period of super-

additivity is very limited. Thus, by 2 minutes, the density produced by the combination is less than the sum produced by the individual agents, while the rate is less than that of the hydroquinone alone. Alternately, if the third criterion is accepted and a density of 2 selected, the rate of the combination will again be less than the sum of the rates of the individual components.

These figures make clear why superadditivity is frequently restricted to the short times of development and support Reinders' and Beukers' statement that the principal action of the methyl *p*-aminophenol is to overcome the induction period of the hydroquinone.

When the activity of the hydroquinone is much less than that of the aminophenol (e.g., Fig. 1a), the increment produced by its addition is slight; but, where its activity more closely approaches that of the aminophenol (Fig. 2a, 3a, and 3b), the increment produced by its addition is greater, that is, greater "superadditivity" is displayed. The relative activity of the separate agents therefore appears to be a reasonably qualitative guide to predicting the increment produced by the combination. Levenson, however, interprets these differences in terms of ease of regeneration of the component agents.^{5,6}

4. *Practical Considerations.* From a practical standpoint, the most important observation is the smallness of the differences obtained between mixtures of the agents, compared with the considerable differences among the several agents. Thus, chlorhydroquinone, used alone, showed advantages over hydroquinone also used alone, in both increased activity and decreased rate of oxidation.¹ However, since the properties of the mixture are determined chiefly by the aminophenol, the combinations containing chlorhydroquinone (with methylaminophenol, II, or the hydroxyethylaminophenol, III) were little more active or aerated little better than those containing hydroquinone and the same aminophenols, and the differences among the several curves of Figures 6b and 7b are small. These differences may not, however, be entirely negligible. Thus, chlorhydroquinone, combined with methyl *p*-aminophenol, requires only 80% the developing time of the usual methyl *p*-aminophenol-hydroquinone combination at a pH of 8.5, which is the approximate alkalinity of the "borax" developers. On the other hand, at a pH of 12.8, hydroquinone shows greater accelerating action and might be preferable for these caustic solutions.

The preceding paper showed certain advantages for the hydroxyethylaminophenol (III) over methyl *p*-aminophenol (II), including (1) low fogging propensity, (2) improved resistance to aerial oxidation in caustic solutions, and (3) increased solubility. The solubility advantage of the hydroxyethyl compound is even more striking in combination with hydroquinone since the

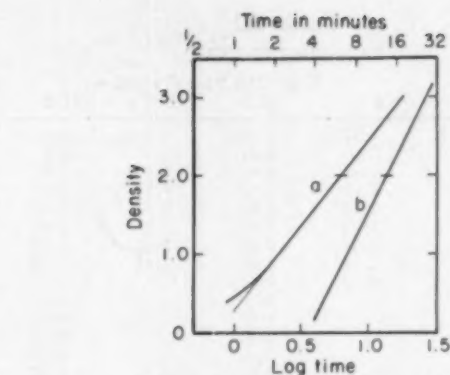


Fig. 9. Curve (a) shows the modification of the developing properties of hydroquinone by the addition of one-tenth the quantity of methyl *p*-aminophenol. The addition has decreased the slope and the induction period.

metoquinone formed with methyl *p*-aminophenol and hydroquinone has very limited solubility, while if such a compound is formed with the hydroxyethylaminophenol, its solubility is apparently very satisfactory. However the other advantages are largely lost, since the methyl *p*-aminophenol by combination, becomes more selective and aerates better.

Altogether, with the few minor exceptions noted above, these experiments would appear to agree fully with the great popularity of methyl *p*-aminophenol (Elon)-hydroquinone combinations. The combination appears to have no disadvantage over either agent alone, is more active, and more highly selective, and is difficult to surpass with any single agent or combination.

Bibliography

1. Henn, R. W., "The Properties of Developing Agents. I. Hydroquinone," *PSA J. Section B (Phot. Sci. and Tech.)* Vol. 18B, pp. 51-55 (1952).
2. Henn, R. W., "The Properties of Developing Agents. II. *p*-Aminophenols," *PSA J. Section B (Phot. Sci. and Tech.)* Vol. 18B, pp. 90-95 (1952).
3. Reinders, W., and Beukers, M. C. F., "Metol-Hydroquinone Developers: The Influence of pH Values and the Proportion of the Mixture," *Phot. J.*, Vol. 74, 76-82 (1934).
4. James, T. H., "The Nonadditive Properties of Elon-Hydroquinone Developers," *PSA J.*, Vol. 9, pp. 62-67 (1943).
5. Levenson, G. I. P., "On the Kinetics of the Reduction of Silver Bromide by Complex Photographic Developers," *Proc. XI Intern. Congr. Pure & Applied Chem.*, London, July 17-24, 1947, Vol. 1, pp. 533-539 (1950).
6. Levenson, G. I. P., "Further Notes on Super-Additive Developers," *Phot. J.*, Vol. 92B, pp. 109-110 (1952).

PHOTOGRAPHIC SCIENCE AND TECHNIQUE

A quarterly technical supplement to PSA Journal

TABLE OF CONTENTS — NOVEMBER 1953

CONFERENCE ON PHOTOGRAPHIC SCIENCE AND TECHNIQUE	ANON	138
A PROCESSING TEST KIT	R. W. HENN AND J. I. CRABTREE	140
PROPERTIES OF DEVELOPING AGENTS. IV. A COUPLING REACTION OF CATECHOLS	R. W. HENN AND D. W. FASSETT	146
PROPERTIES OF DEVELOPING AGENTS. V. AMINOPHENYLPHENOLS. AN AUTOCOUPLING REACTION	R. W. HENN	149
METHODS OF ELIMINATING THE IMAGE ON ONE SIDE OF DOUBLE-COATED X-RAY FILM	H. F. SHERWOOD	151
THE USE OF PHOTOGRAPHY IN DETECTING AND PROVING VOTE FRAUDS	JOSEPH THOLL	152
MECHANISM OF SUPERADDITIVITY IN PHOTOGRAPHIC DEVELOPMENT	T. H. JAMES	156
PHOTOGRAPHY IN COMBUSTION STUDIES	HARRY WILLIAMS AND A. GREENVILLE WHITTAKER	161
NEW STANDARDS FOR PHOTOGRAPHY	CAROLYN LOCHER	162
PROPOSED AMERICAN STANDARD SPECIFICATIONS FOR PHOTOGRAPHIC FILTER SIZES		165
PROPOSED AMERICAN STANDARD FOR THE INTERNAL SYNCHRONIZATION OF FRONT SHUTTERS		167
DEVELOPERS FOR USE IN DETERMINING THE DISTRIBUTION OF THE LATENT PHOTOGRAPHIC IMAGE	T. H. JAMES, W. VANSELOW, AND R. F. QUIRK	170
AN APPLICATION OF MICRO-FLASH PHOTOGRAPHY TO EXTERIOR BALLISTICS PROBLEMS	DONALD R. BERESFORD	172
TITLE PAGE FOR BINDING VOLUME 19B AND INDEX FOR 1953		175



EDITORIAL

The first issue of PHOTOGRAPHIC SCIENCE AND TECHNIQUE appeared in January 1950. The present issue, the sixteenth to appear, completes Volume 19B and ends four years of publication as the quarterly Section B of the PSA Journal.

The Board of Editors, provided by the Technical Division, after dealing with the problems inherent in a new venture, consider the publication well established. The editors who have worked tirelessly and unselfishly are grateful for the support received from 128 authors and contributors, from the important research laboratories, engineering groups, and educational institutions active in the field of photography.

Establishing in North America a journal to serve photographic scientists, engineers, and the technical people in many endeavors who use photography in their work has been a source of satisfaction to President Harkness and to the Society in carrying out the aims of PSA to serve photography in all its aspects.

The Board of Directors has decided now to publish PHOTOGRAPHIC SCIENCE AND TECHNIQUE independently rather than issue it as Section B of the PSA Journal. The first 1954 issue, therefore, will be Series II, Volume 1, Number 1 and it will be mailed quarterly to subscribers, exchange publications, and to Society members who request it.

CONFERENCE ON PHOTOGRAPHIC SCIENCE AND TECHNIQUE

On May 16 at Manchester University the Scientific and Technical Group of the Royal Photographic Society held a Conference on photographic science and technique. The conference was opened by Dr. G. N. Burkhardt of the Science Faculty of Manchester University. The Chairmen of the morning and afternoon sessions were Mr. V. Gallafent (R.P.S. Scientific and Technical Group) and Mr. C. W. Bradley (British Cotton Industry Research Association).

The first paper was not directly related to photography, but dealt with the legibility of print when projected from 3 1/4-inch square lantern slides. This is a matter of importance to

audiences particularly at scientific meetings for as the speaker, Dr. R. Ollerenshaw, (Manchester Royal Infirmary) pointed out there is evidence that the average eyesight of undergraduates is inferior to that of the 18-year old National Service entrants, and deteriorates during University residence. Whatever the form of the lettering, the illumination of the screen should be high, the contrast between the lettering and background strong, and preferably with the letters white on black, according to Dr. Ollerenshaw. The greatest distance at which members of the audience should be seated should be six times the width of the screen (owing to the limited acuity of the eye) and the

FOURTH 1953 ISSUE ☆ VOLUME 19B, NUMBER FOUR ☆ PUBLISHED WITH THE PSA JOURNAL FOR NOVEMBER 1953

PHOTOGRAPHIC SCIENCE AND TECHNIQUE BOARD OF EDITORS

EDITOR, PAUL ARNOLD, APSA, Hon. PSA
26 Hotchkiss Street, South Binghamton, N. Y.

ASST. EDITOR, H. LOU GIBSON, FPSA
343 State Street Rochester 4, New York

MORRIS GURRIE, APSA 5412 N. Bernard Street
R. C. HAKANSON 10322 Lake Shore Boulevard
HUTCHINSON HOWELL 700 Commonwealth Avenue
LAWRENCE B. FRAIR P.O. Box 1009 Rochester 3, New York
Chicago 25, Ill.
Cleveland 8, Ohio
Boston, Massachusetts
PETER KRAUSE, APSA 69 Bourndale Road, South Manhasset, New York
HERBERT MEYER 1421 Northwestern Avenue Hollywood 27, Calif.
JOHN B. TAYLOR 118 Laurel Avenue Binghamton, New York

PHOTOGRAPHIC SCIENCE AND TECHNIQUE is an official organ of the Photographic Society of America dedicated to the publication of scientific and technical papers dealing with the theory and practice of photography. Its aim is to encourage the publication of authoritative articles describing original research, techniques, and the engineering aspects of new equipment in all fields of photography. It is intended to interest and inform the advanced amateurs, the professionals, the technologists, and the scientists who study or apply photographic processes.

Prepared four times yearly by the Technical Division, PHOTOGRAPHIC SCIENCE AND TECHNIQUE is published as SECTION B of the PSA JOURNAL. The issues are separately numbered and page numbered and indexed annually.

Society memberships, including subscriptions to both publications, may be obtained from PSA Headquarters, 2005 Walnut Street, Philadelphia 3, Pennsylvania, upon payment of \$10.00 annual dues. Separate subscriptions are not available, except institutional and library subscriptions at \$5.00 a year. No extra charge is made for mailing to foreign countries.

Address all manuscripts and communications to the Editor. Unacceptable manuscripts will be returned promptly. No responsibility is assumed for the accuracy of statements by contributors but attempts will be made to avoid the publication of errors. The contents will be protected by domestic and foreign copyright and may not be reproduced without the written permission of the editor. The publishing of opinions expressed by authors does not necessarily indicate concurrence or endorsement by the editors, by the Technical Division, or by the Photographic Society of America.

nearest distance twice the width of the screen (otherwise a tiresome rotation of the head itself must supplement the normal movement of the eyes). The seats should be grouped within a triangle of 60° angle at its apex at the centre of the screen.

A study of printers' type faces shows that upper case Gill Sans Boid is best for acuity, readability, and speed of reading. The italic form is useful for ordinate legends to graphs. The individual characters should be not less than 2 mm. high on the slide, and lower-case type should be used only when this condition can be met. It has been found best to do all lettering with a small printing press, a process which is at least as quick as good stencilling. The gap between lines of type should be equal to the body height of the type and, as far as possible, each line should carry one item of the message. Diagrams and lettering in journals and books cannot well be used for lantern slides, nor vice-versa.

Mr. P. C. Smethurst (Smethurst High-Light Ltd., Bolton) discussed the use of supplementary lenses with a telecentric stop. If a positive supplementary lens is arranged so that its rear principal focus is at the front nodal point of the camera lens, all the principal rays in the object space are parallel to the axis. The photograph then displays perspective such as would be obtained if the objects photographed were at infinity, and all measures of size on it are relatively correct whatever the distances of the objects. The same device thus avoids the necessity for exact location of objects along the axis when it is important to measure sizes. Variations in perspective are obtained by placing the supplementary lens at other positions along the axis, so that the pencil of principal rays in the object space is divergent or convergent. A double system, sometimes useful, is obtained when a supplementary lens (a telescope objective) is used in the same way on each side of a camera objective.

Mr. F. Wardlaw (Christie Hospital, Manchester) described illumination of deep and narrow cavities by means of a concave mirror reflecting light from a lamp set to one side. Photographs are taken through a central aperture in the mirror, the subject being observed by means of a two-mirror periscope of which the first mirror is a thin sheet of unsilvered glass. The aberrations of a concave mirror used at an angle help to smooth out the image of the lamp filament and for the same reason high optical quality is not necessary, but care should be taken to keep light off the front edges of the cavity by suitable focusing.

Dr. H. J. J. Braddick (Dept. of Physics, University of Manchester) pointed out that the photography of tracks in cloud chambers involved contradictory requirements. For example, the minimum delay between the arrival of a particle and the expansion is 10 milliseconds. Then a period up to 250 milliseconds is required for the water drops to grow. The shorter this period can be the more nearly will the water drops represent the particle track, but the longer they are allowed to grow the brighter will the track be. It is of course difficult to get adequate illumination because the camera lens must be stopped down to get a fair depth of the chamber sharp in the photograph. In order to get adequate illumination, high power flash tubes or heavily over-run tungsten lamps are used. If the inevitable delay between the arrival of a particle and the expansion is increased, and an electric field is established across the chamber, the positive and negative ions separate, forming two parallel tracks from the intensities of which the relative concentrations of ions of the two signs may be estimated. This technique is not possible with nuclear track plates.

Mr. J. V. Major (University of Manchester) discussed the distortion of tracks in plates for recording nuclear particles. Measurements indicate that there are two components, one

centrally symmetrical and the other like a shear across the plate. Uneven drying (from the edges inwards) can account for part of the distortion, but the origin of the remainder is not clear. Temperature gradients during development may be responsible.

Mr. E. W. H. Selwyn (Kodak Limited) discussed progress of the physics of the developed image. Our qualitative knowledge of the make-up of the characteristic curve, of granularity, graininess, resolving power and sharpness is fairly good, said the speaker, though there are still outstanding problems, and little quantitative information is available.

Mr. J. S. Courtney-Pratt (University of Cambridge) described methods of high speed photography based on dissection of the image. If a plate embossed with a large number of lenses is placed near the focal plane of a camera a series of images of the camera lens will be formed on the sensitive material, and these taken altogether form a picture of what is in front of the camera, rather like a half-tone illustration. When a small aperture is moved across the camera lens a continuous line of overlapping small images is formed behind each element of the lenticular screen, thus recording any movement in the objects in front of the camera. In practice a series of apertures is used, like the original Baird scanning disk for television, and each lenticular element produces a "raster." The fundamental advantage of this system is that the speed of the scanning disk, being simple rotation, may be made very high and with bright enough (e.g. self-luminous) subjects records may be obtained at the rate of 4 million per second. The same system reversed may be used for "unscrambling" in slow motion or statically.

Mr. C. Burns (British Iron and Steel Research Association) described how the problem of recording the very fast motion of lumps of material swirling around in the hollow just beyond the tuyeres in blast furnaces was dealt with. Stereoscopic motion pictures were made using two ports into a tuyere and a mirror system to produce the necessary pairs of pictures side by side on each frame of a 16mm. film. When the pictures are projected, individual lumps of material can be recognised, against the very heterogeneous background. The location (along the axis of the tuyere) is measured by a quadruple projector arrangement of which the movements are linked. First one pair of beams are made to coincide on some fixed detail in the tuyere, one on each of the projected pictures. The other two beams are then made to cross in space at the distance of the fixed detail in question and the second pair of beams locked to the first pair. If the first pair of beams are now made to coincide with some other detail, the second pair follow their movements and intersect in space at the original distance of the new detail.

Mr. A. J. Insull (Shell Petroleum Co., Thornton le Moors) described the functions and some of the equipment of an industrial photographic section of a laboratory.

One of the most important duties of such a section is to be able to repeat record photographs exactly, for which purpose arrangements must be made to locate any object precisely, to be able to duplicate the lighting arrangements and to be able to set the camera to given conditions.

Records of all these settings must be kept, for it is commonly the case that photographs, for example of pistons, require to be repeated, for comparison to be made to detect changes, sometimes at long intervals. Artistic quality (but *not* the technical quality) is usually unimportant, so that for recording deposits on elements of mechanisms, for example, use may be made of completely diffused lighting. Colour photography is very useful in such cases, since the additional information (on the colour) is valuable.

A PROCESSING TEST KIT*

R. W. Henn and J. I. Crabtree

ABSTRACT

A kit for determining the condition of the short stop and fixing solutions used in the processing of black-and-white films and papers and the permanency of the final print is described. The condition of the stop bath is evaluated with indicator papers. The film fixing bath is checked with regard to acidity and clearing time, while the discard point of the print fixing bath is based on its silver content, which is determined with potassium iodide. The hypo content of the processed print is measured by the stain produced with acid silver nitrate, and the silver content is measured by staining with sodium sulfide.

THIS PAPER describes a testing procedure for determining the condition of the stop bath and fixing bath, and also for determining the thoroughness of the processing of the final print or film. The testing of the developer solution is a complex problem and has not been included in this article. In the present state of our knowledge, the condition of a developer can be determined satisfactorily only through photographic tests which must include a standard reference developer solution. The tests described below, on the other hand, are complete in themselves.

Periodic testing of processing solutions is essential if films and prints of good quality are to be obtained, and it is equally important to test the finished prints in order to be assured of their permanency. Few photographers are trained chemists, but with the Test Kit described here, an adequate evaluation of the stop bath and fixing bath and the thoroughness of processing can be made in the absence of a detailed knowledge of chemistry.

I. Testing the Stop Bath

The stop bath serves a threefold purpose in the processing of films and prints. It stops development, thus controlling the contrast, density, and uniformity of the image; it preserves the acidity of the fixing bath, keeping it free from sludging, as well as maintaining its hardening properties; and it prevents stains, both those due to oxidized developer and those due to dichroic silver.

A film stop bath must be kept strongly acid for maximum efficiency in order to neutralize rapidly the alkali in the developer carried over and to arrest development immediately. The bath should be at a pH value of 5.0 or lower; but, except when freshly mixed, the pH should not be below 4.0, for the following reasons: A bath which is too acid will tend to cause blisters in the negative if the developer contains carbonate, while an excess of acid carried over into the fixing bath may cause sulfurization. A paper stop bath need not be quite so acid, being effective up to a pH of about 5.5.

The condition of such stop baths may be checked with indicator dye solutions, bromocresol green being a suitable indicator for the film stop bath, and bromocresol purple, for the paper stop bath. However, it is more convenient to employ test papers, and at least two papers which are satisfactory are commercially available and are listed in Table III.

Making the Test

(a) *Film Stop Baths.* Immerse a strip of test paper No. 1 in the well-stirred stop bath. Observe the resulting hue of the test paper (under daylight or bright artificial light but not a safelight) and compare it, while wet, with the reference chart on the test-strip bottle. When immersed in a freshly mixed bath, a strip of the test paper is yellow, but during the greater part of the useful life of a stop bath, the strip shows a green color. A definite blue color indicates the need of replenishment, whereas a definite yellow color indicates a strongly acid condition.

(b) *Print Stop Baths.* Immerse a strip of test paper No. 2 briefly in the well-stirred stop bath. Observe the resulting hue of the paper. Under a Kodak Wratten Series OA safelight, the strip appears light in color if the bath is in satisfactory condition, dark if it is exhausted. If working in bright artificial light, or daylight, compare the resulting hue, while wet, with the reference chart on the test-strip bottle. A strip of the test paper for print stop baths will appear yellow in a freshly mixed bath. A red-violet color indicates exhaustion, and the bath should be discarded.

Discussion

This test applies only to the acetic acid type of stop bath and does not apply to chrome alum stop baths or to alkaline stop baths employed in color photography.

An understanding of the acetic acid system in question is promoted by a study of Figures 1 and 2, which are reproduced from an earlier paper.¹ Figure 1 shows the strong buffering action of acetic acid in the pH range of 4 to 5, while Figure 2 shows how successfully a bath may be maintained in this range by appropriate replenishment.

II. Testing the Fixing Bath

A fixing bath may become exhausted for one or more of the following reasons: (1) it may cease to fix out the undeveloped silver halide from the emulsion, within a reasonable time, owing to excessive dilution of the thiosulfate and to the accumulation of silver and of iodide in the bath; (2) the concentration of silver thiosulfates may become excessive so that even though the silver halides are dissolved, excessive silver is retained by the emulsion after washing which will decompose eventually on storage, or more immediately on toning, to produce stains; and (3) the acidity may be lost so that the bath stains or sludges or fails to harden.

* Communication No. 1572 from the Research Laboratories, Eastman Kodak Company, Rochester 4, N. Y. Received 7 May 1953.

The last factor, loss of acidity, is not ordinarily a problem when an acid stop bath is employed. If only a water rinse is used, the acidity of the fixing bath may be checked with the same bromocresol green paper as used for the film stop bath.

When the acidity of the film fixing bath is maintained, the chief limitation to its life is its ability to clear and fix film within the period that the process can tolerate. However, a different criterion applies to paper fixing baths. Here, the accumulation of silver is serious, and will ordinarily be a potential cause of difficulty before the bath has lost its ability to "clear" actively.

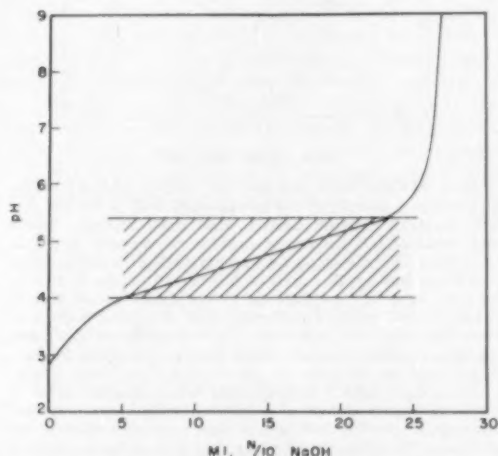


Fig. 1. NEUTRALIZATION CURVE OF ACETIC ACID WITH SODIUM HYDROXIDE. The buffer range is shown by the shaded area. In this range a considerable quantity of the alkali may be added without greatly changing the acidity (pH). Data are for a 25-ml. sample of 0.6% acetic acid neutralized by 0.1N sodium hydroxide.

In the tests described below, the activity of the film fixing bath is measured directly by observing the time to clear test-film strips, while the silver content of the print bath is measured with a solution of potassium iodide. Two variations of the silver test are given, in which the formation of a precipitate occurs at approximately (a) 1.0, and (b) 0.5 gram of silver per liter of fixing bath. The higher level is entirely acceptable for many applications and corresponds to an exhaustion by processing possibly eighty 8- x 10-inch prints of average silver content per gallon. The lower level corresponds to more severe standards and is employed where the print is to be kept for long periods, is to be toned, or when only short washing times are available. In this case, effective silver removal with reasonable economy of material is obtained by the use of two successive fixing baths.²

Making the Test

(a) *Film Fixing Baths.* Select an emulsion of the type which will be employed with the fixing bath. Kodak Verichrome roll film is suitable as a test film for most baths, but in special cases, x-ray films, positive

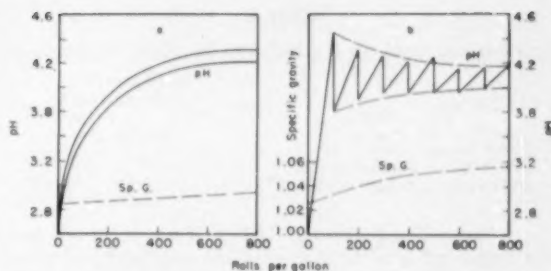


Fig. 2. LABORATORY EXHAUSTIONS. In Curve (a), Stop Bath SB-5a was replenished frequently with 10% acetic acid, while in Curve (b) replenishment was less frequent, and 56% acid was used. pH values obtained before and after replenishment are plotted. The specific gravity is a measure of the salt content, and consequently of the antiswelling action of the bath.

films, etc., may be desirable. This film is cut into strips, which need not be large, $\frac{1}{2}$ x $3\frac{1}{2}$ inches being suitable; and this size can be cut off the unexposed end of a roll of film. Immerse one fourth the length of this film in the fixing bath for approximately 15 seconds, then start the timing and immerse the remainder of the strip. Agitate gently to correspond to the agitation given during normal fixation. The portion immersed first becomes entirely clear and serves as a guide to allow exact determination of the time at which the remainder of the strip clears.

Verichrome film will ordinarily clear in freshly mixed sodium thiosulfate baths such as Kodak F-5, F-6, Kodak Acid Fixer, and Kodak Photofix in about 2 minutes, and in rapid baths such as Kodak Rapid Liquid Fixer and Kodafix Solution in about 40 seconds. As the baths are exhausted, these times rise to about 4 minutes for the sodium thiosulfate baths and to about 2 minutes for the rapid baths, resulting in total fixing times of about 8 and 4 minutes, respectively. At this stage they should be discarded, or replenished according to published recommendations, although if long fixing times are available, as in special equipment, the life may be further extended.

(b) *Print Fixing Baths.* 1. "Normal" Standard. (For use where a slight over-all yellow stain would be tolerable after long storage.) Place 5 drops of 20% potassium iodide solution in a small test tube or vial. Add 5 drops of fixer, mix, and then add 5 drops of water. If a permanent, yellowish-white precipitate appears, the bath is exhausted. Any slight milkiness should be disregarded.

2. "Quality" Standard. (For use with the second bath of a two-fixing bath system or where only very low stain levels are tolerable.) Place 5 drops of the 20% potassium iodide solution in a small test tube or vial. Add 5 drops of fixer, then 15 drops of water, and mix. If a permanent, yellowish-white precipitate appears, the bath is exhausted. Any slight milkiness should be disregarded. If this is the second bath of a two-bath system, it need not be discarded but will still serve satisfactorily as the first bath of such a system and may be so employed.

Table I

CLEARING TIME AS A FUNCTION OF TEMPERATURE

Fixing Bath	Seconds to Clear Verichrome Film at:	
	68 F	80 F
Kodak Rapid Liquid, Fresh	35	27
Kodak Rapid, Exhaustion No. 1	130	110
Kodak Rapid, Exhaustion No. 2	75	52

(c) *Acidity Test for Fixing Baths.* If no stop bath has been employed or if the acidity of the stop bath is doubtful, the acidity of the fixing bath should be checked, employing the paper used for testing the film stop bath (test paper No. 1). If the hue of this paper is green, the bath is in satisfactory condition; if it is blue, the fixer should be discarded.

Discussion

The fact that the *silver content* of the film fixing bath is relatively unimportant in relation to washing was shown in a series of experiments using baths from actual exhaustion trials and synthetically prepared baths containing up to 8 grams of silver per liter. After washing, the silver retained by the films fixed in the exhausted baths was only slightly greater than that of films fixed in the fresh baths and usually produced net stain densities (on sulfiding) of less than 0.10. On the other hand, prints fixed in silver-laden baths retained both more silver and more hypo, as shown in Figure 3, which is reproduced from a previous paper on two-bath fixation.²

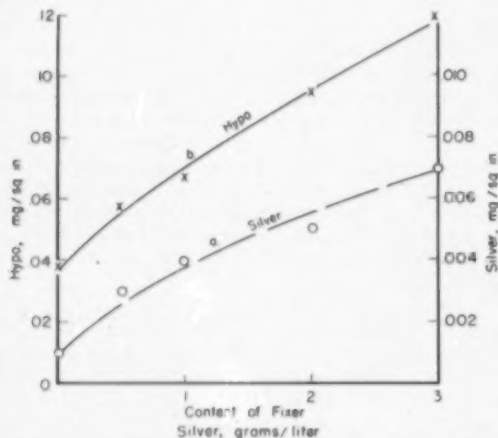


Fig. 3. (a) HYPO AND (b) SILVER CONTENT OF THE PRINT AS A FUNCTION OF THE SILVER CONTENT OF THE FIXING BATH. Note how both the hypo and silver retained in the print increase with the silver content of the fixer.

The clearing test employed for the film fixing bath is dependent on the *agitation*, the *temperature*, and to some slight extent (as it affects agitation) on the nature of the vessel employed. The effect of agitation is not great for a fresh bath, a variation in the "time to clear" of only 20% having been found in one series. However, unagitated films have been found to clear only very slowly in excessively exhausted baths. The fix-

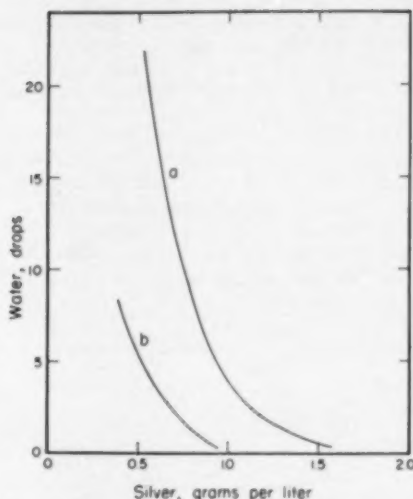


Fig. 4. IODIDE TEST FOR SILVER: EFFECT OF DILUTION. In this test 5 drops of the fixing bath and 5 drops of a 20% solution of potassium iodide were mixed. Then water was added dropwise until a permanent precipitate occurred. Curve (a) was obtained with the Kodak Acid Fixer but applies also to Kodak Photofix, F-5, F-6, and F-24, and to 1:3 dilutions of both the Kodak Rapid Liquid Fixer, with Hardener, and Kodafix Solution. Curve (b) was obtained with a 1:7 dilution of Kodafix, and also applies to other dilute fixers, including Photofix 1:1, and to the fixer of the Kodak Tri-Chem Pack. A fixing bath which precipitates when diluted with 5 drops of water shows a measurable, but not intense, staining propensity, while one that precipitates only on dilution with 15 drops of water shows very little staining propensity.

ing reaction is dependent on temperature, although less so than is development, and the temperature of the test should be within 5 F of that at which the bath is to be employed. The degree of temperature-dependence is illustrated by the examples of Table I.

Some question may be raised as to the merits of employing test strips to determine the clearing time as compared to observing directly the clearing of the film being processed. The latter method is, of course, entirely suitable, but it is not always convenient to observe the clearing process, and such observations may occasionally cause fogging of the film. Furthermore, the test strips form a quantitative measurement which may be recorded to follow the behavior of the bath during its entire life. Such a record is especially useful when employing a replenishment system.

The *potassium iodide test* for silver in the fixing bath involves a three-component system, in which the silver is held in solution either as the double thiosulfate salt or as the double iodide ion, or precipitated as silver iodide, according to the relative concentrations of the several ingredients. The test has been described casually in the photographic literature,³ but no quantitative information has been published. However, by adjusting the strength of the iodide solution and varying the quantity of fixing bath added, the iodide test may be made to respond to a wide range of silver concentrations. Thus, in Figure 4 it is seen that when working in the proportion of 5 drops of fixer to 5 drops of the 20%

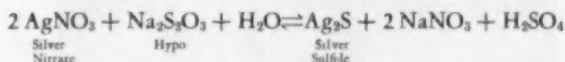
iodide solution, a test could be obtained at any silver concentration between 0.5 and possibly 1.5 grams per liter, according to the quantity of diluting water employed. If higher concentrations of silver are to be determined, it is necessary to increase the concentration of the iodide solution and its relative volume.

The formation of the precipitate is dependent not only on the iodide and silver concentrations, but also on the thiosulfate concentration; and the more dilute the fixing bath, the lower will be the silver concentration at which the precipitation occurs. Thus, the 1:7 Kodafix Solution of Curve b, Figure 4, precipitates at about half the silver concentration of the more concentrated baths. This is fortuitous, because prints processed in the more dilute baths also display hypo-retention and silver-staining propensities as is shown in Table II, in which 1:3 and 1:7 dilutions of Kodafix Solution are compared. It would appear that the iodide test does more than merely measure the silver concentration in the fixing bath; it measures the silver:thiosulfate ratio, which, in turn, determines the ease with which the silver thiosulfate is removed by washing, and therefore, the staining potentiality of the bath.

III. Testing the Processed Prints

The physical quality and permanence of a processed paper print is dependent not only on the condition of the processing solutions, but also on the completeness of the washing process. The function of washing is to remove (1) the thiosulfate (hypo) absorbed from the fixing bath, and (2) any remaining non-image silver, which will now be present as a complex silver thiosulfate. These are unstable compounds which eventually decompose to (a) sulfide the image (cause "fading"), or (b) produce an over-all yellowish-brown stain of silver sulfide, most noticeable in the highlights.

These two unstable compounds, hypo and silver salts, are most conveniently and directly detected by treating the prints with reagents which will change them to brown silver sulfide, and estimating the density of this sulfide deposit. In the case of hypo, the reagent is silver nitrate, which is made slightly acid to stabilize it against reaction with alkali and sulfite which might be present. Reaction of the silver nitrate and hypo produces silver sulfide according to the following equation:



The presence of silver salts is determined by treating the prints with sodium sulfide.

The intensity of the stain will be proportional to the concentration of hypo or silver thiosulfate present. The yellowish-brown silver sulfide stain obtained in the hypo test is always more intense than that obtained in the silver test. However, an appreciable amount of hypo must be retained in a print before serious fading will occur, whereas the density of the stain obtained on testing for silver thiosulfate directly indicates the discoloration that will occur eventually. Since the hypo and the silver salts are distributed throughout the base as well as the emulsion, the total quantity present is

Table II

HYPO AND SILVER CONTENT OF PRINT AS AFFECTED BY THE HYPO CONTENT OF FIXER

Fixer: Kodafix Paper: Velox F-3 Washing: 30 min. at 65-70 F.

Dilution	Fixing Bath	Washed Print	
	Silver Content (Grams per Liter)	Hypo Content (Mg. per Sq. In.)	Silver Content (Stain Density)
1:3	0	0.036	0.12
1:3	2	.066	.18
1:7	0	.057	.16
1:7	2	.116	.20

best determined by reading the transmission density (preferably blue), but this is often inconvenient. In the test described below, the density of the stain is estimated by reflected light, which gives a valuable guide, subject to the conditions discussed.

Making the Tests

(a) *Hypo*. After washing, wipe the excess water from the face (emulsion side) of a blank piece of the same photographic paper, processed with the batch of prints (or from the extra margin area of one of the prints). Place one drop of the test solution HT-2 on the face of this processed paper sample. Allow the solution to stand for 2 minutes, then rinse to remove the excess reagent.

The density of the resulting stain will be roughly proportional to the residual hypo content. Satisfactorily washed prints do not show more than a very light brown (tan) stain. The density of this stain is best determined by comparing it with a suitable standard. Such a standard is found in the stain patches published by the Eastman Kodak Co. in the booklet, "Permanence of Negatives and Prints."

(b) *Residual Silver*. The same technique of spotting a blank print or spare margin is used, but in this case the silver test solution, Kodak ST-1, is employed. Any color darker than a just-visible cream tint indicates an objectionable excess of residual silver compounds.

Discussion

1. *Background of the Tests*. The silver nitrate test for hypo has been described in detail by Crabtree, Eaton, and Muehler,⁴ who also mention the sulfide test for silver. The silver nitrate test is the basis for a photographic standard approved by the American Standards Association.⁵

2. *Permissible Hypo Concentration*. This will depend on the period for which the print is to be kept, the conditions of storage, the degree of fading tolerable, and the nature of the emulsion. It is usually unsafe, however, to assume that a print is of only temporary importance, and it should therefore be washed sufficiently to be good for many years.

If the print is to be kept under moist conditions, as in a damp basement, and especially under warm, moist conditions, as in the tropics, its life may be a fraction of that otherwise anticipated. A slight fading or toning may perhaps be tolerated under some conditions, as with a copy of printed matter, provided the legibility is not impaired, but normally it is very objectionable.

Table III
TEST MATERIALS AND FORMULAS

I. pH PAPERS			
Paper No.	Name	Manufacturer	Dealer
1	Precision pH Paper No. 3656 OR Accutint pH Paper No. 70	Precision Labs., Rossmyrne, Ohio	Harshaw Scientific Co., Cleveland 6, Ohio
		Annachemia, Montreal	Will Corp., Rochester 3, N. Y.
2	Precision Paper No. 4662 OR Accutint Paper No. 80		
2. POTASSIUM IODIDE SOLUTION			
Potassium iodide	Metric 20.0 grams	Avoirdupois and U. S. liquid 2 ounces	
Water to	100 cc.	10 ounces	
3. ACID SILVER NITRATE SOLUTION, KODAK HT-2			
Water	750 cc.	24 ounces	
Silver nitrate	7.5 grams	1/4 ounce	
Acetic acid, 28%	125.0 cc.	4 ounces	
Water to	1000 cc.	32 ounces	
Keep in a brown bottle, away from light			
4. SODIUM SULFIDE SOLUTION, KODAK ST-1			
Water	100 cc.	4 ounces	
Sodium sulfide	2.0 grams	36 grains	
Keep in a well-stoppered bottle; replace monthly			

The degree of fading is also very dependent on the nature of the emulsion. Most enlarging papers, such as Kodabromide, and many contact papers, including Velox, tolerate considerable hypo (0.10 to 0.20 mg. per sq. in.), but fine-grain portrait papers, such as Kodak Platino and Kodak Opal, may fade when the hypo content is as low as 0.05 to 0.10 mg. per square inch.

The tolerable silver content is similarly dependent on the duration of storage and the conditions of humidity and temperature; but it is almost independent of the nature of the emulsion. In the long run, the stain will tend to reach the level shown by the spot test, and, therefore, a silver content should not be tolerated which will produce a high stain in this test. If the paper is toned, as with polysulfide, the stain will develop immediately.

3. *Imperfections of the Hypo Spot Test.* The test estimates only the hypo in the emulsion layer of the print, but any hypo in the base may likewise contribute to fading. If the test solution is applied to the base side of the print, the stain is usually less dense than that obtained on the emulsion side; hence the preference for the emulsion-side test.

However, many hypo elimination systems (including the use of alkalis, salts, and peroxide-ammonia) remove a more-than-proportional share of hypo from the emulsion layer so that a test on the face side may show less stain than if it had been made on the base side and would, therefore, be misleading. In such cases, the print should be immersed in the test solution and the resulting stain evaluated by measuring the transmission density.^{4,5}

The stability of the residual hypo in the emulsion is a function of its environs. Specifically, hypo is more stable in an alkaline medium than in an acid one, so that more hypo is tolerable when the traces of acid fixer left

in the print have been neutralized by subsequent alkaline treatment (e.g., by bathing in an alkaline washing accelerator such as sodium carbonate or metaborate).

A moist incubation test will produce the equivalent of years of normal aging and predict the behavior of the emulsion in question. An image containing fine detail of moderate density is the most sensitive. This is incubated for two weeks at 110 F (43 C) and 90% relative humidity (established with a saturated potassium sulfate solution). An image stable under this test is considered entirely satisfactory for any normal storage. The incubation test is, of course, impractical for batchwise checking of processing, but is of great value in establishing a washing procedure that will give permanent prints.

4. *Hypo Test for Films.* The silver nitrate spot or dip test described can be applied to films, the density of the stain increasing with increasing hypo content. Only a very light brown stain is tolerable with fine-grain positive and archival materials, but a somewhat denser stain may be tolerated with coarse-grained negative emulsions.

Where an exact measure of hypo content is desired, the mercuric chloride test of Crabtree and Ross is to be preferred. (This test is described in References 4 and 6.) It demands the preparation of a set of standards or a photoelectric calibration, either of which is inconvenient for many photographers, but processors of microfilm or other material for archival purposes should be fully acquainted with this test or have the condition of the film checked by a competent laboratory using the mercuric chloride test.

Summary of Tests

Figure 5 pictures an assembled kit for performing the tests which have been outlined in the preceding discussion, and Table III gives the composition of these materials. The pH papers pictured are the "Precision" series, the "Accutint" group being packaged somewhat differently. The dealers listed for these papers are



Fig. 5. AN ASSEMBLED TEST KIT. This kit contains: (1) and (2) the indicator papers for testing the stop baths, (3) the film strips for testing the film fixer, (4) the iodide solution for testing the print fixer, (5) and (6) the silver nitrate and sulfide solutions for testing the washed prints, and (7) and (8) droppers and vials for carrying out the test of the print fixing bath. These reagents are shown in clear glass vials, and mounted in a Plexiglas plastic base. However, reagents (3) and (5) should be shielded from the light, while wood or other plastics are very suitable for the stand.

Table IV

SUMMARY OF TESTS

Solution	Test For	Method	Indication	Significance
Film Stop Bath	pH	Paper No. 1	Yellow Yellow-green Green Blue-green Blue	Fresh, pH = 3-4 Adequately replenished, pH = 4 Working range, pH = 4-5 Doubtful, pH = 5 Exhausted, pH = 5+
Print Stop Bath	pH	Paper No. 2	Yellow Bronze Purple	Satisfactory, pH = 3-5 Doubtful, pH = 5.5 Exhausted, pH = 6
Print or Film Fixing Bath	pH	Paper No. 1	Green Blue	Satisfactory, pH = 4-5 Exhausted, pH = 5+
Film Fixing Bath	Clearing Time	Film Strips	Excessive Time = 2X or 3X that of fresh bath	Discard or replenish (fix for twice the time to clear)
Print Fixing Bath	Silver Content	Potassium Iodide Solution	Cloudy	Discard or, if two-bath, advance
Print	Hypo Content	Acid Silver Nitrate	Brown Stain	Only very slight stain acceptable
Print	Silver Content	Sodium Sulfide Solution	Brown Stain	Only very slight stain acceptable

Table V

REPLENISHMENT OF SOLUTIONS

Solution	Typical Formula	Replenishment Interval*	Solution	Quantity**	Discard Point*
Film Stop Bath	Kodak SB-5a	40	28% Acetic Acid	5 ounces	560
Print Stop Bath	Kodak SB-1	40	28% Acetic Acid	3 ounces	160
Film Fixing Bath	Kodak Rapid Liquid Fixer, with Hardener	40	Stock Solution A + Stock Solution B	5 1/4 ounces A + 3/4 ounce B	560
Print Fixing Bath (2 successive baths)	Kodak F-6	200	Advance 2nd bath to replace first		1000 (Replace both baths)

* Expressed as 8- x 10-inch films (or prints) per gallon.

** A replenishment rate of 1 ounce per gallon is equivalent to 7.5 cc. per liter.

representative only, and the manufacturer may be consulted for a complete list.

The film strips are shown in a clear glass vial, and the solutions in clear glass bottles. However, both the film strips and the silver nitrate solution (No. 3 in this picture) should be protected from excessive light. The tubes pictured are "shell" vials, which are of convenient length, but small test tubes will function effectively. The pipettes or "medicine droppers" are to measure the drops of fixer and water used in making the iodide test. The glassware must be rinsed well immediately after use to avoid stubborn deposits of silver iodide and of sulfur. If the tubes do become cloudy from a deposit of silver iodide, they may be cleaned by immersion in a fresh fixing bath.

The formulas employed are also given in Table III. The sulfide solution corresponds to the Kodak ST-1 formula, but the method of use is somewhat different in that, for convenience, we do not suggest further dilution before use. Since sodium sulfide may in itself, particularly if impure, produce a little stain density, the more exacting workers may prefer to dilute the solution 1:9 with water before making the test. However, since the keeping properties of the dilute solution are poor, it will need to be freshly prepared.

Table IV summarizes the testing procedures, and the significance of the various responses. For example, the film stop bath is to be kept in the "green" range, the paper stop bath in the "yellow" range, etc. This table is intended only as a summary; in order to perform each test intelligently, it is necessary to read the more detailed description given in the body of the paper.

If a test indicates that the bath is in good condition, its use may normally be extended, even beyond the "capacity" figure published for the solution, since its actual capacity will vary greatly with the conditions of use. However, if the test indicates exhaustion, or approaching exhaustion, the bath should be discarded or replenished. Table V includes replenishment figures for a number of baths. The frequency of replenishment and the quantities used have been set high enough to allow for quite severe processing conditions, and, when processing under other conditions, especially if an appreciable (5 seconds) draining period between baths is employed, or if work is done under favorable fixing or washing conditions, these figures may be extended materially with resultant economy, provided always that the test is made accurately. The results must, of course, be used intelligently, and if the bath becomes unusable from some secondary reason such as accumulation of sludge or lack of hardening in a fixer, it should be discarded regardless of its silver content, activity, or pH value.

References

1. Henn, R. W., and Crabtree, J. I., "Replenishment of the Film Stop Bath," *PSA J. (Phot. Sci. & Tech.)*, Vol. 17B, pp. 13-18 (Feb. 1951).
2. Crabtree, J. I., Henn, R. W., and Edgerton, R. F., "Two-Bath Fixation of Prints," *PSA J. (Phot. Sci. & Tech.)*, Vol. 19B, pp. 10-15 (Feb. 1953).
3. "Fixierbadprüfung," *Fot. Rund.*, Vol. 74, p. 33, (Jan. 1937); *Brit. J. Phot.* Vol. 84, p. 104 (Feb. 12, 1937).
4. Crabtree, J. I., Eaton, G. T., and Muchler, L. E., "A Review of Hypo Testing Methods," *J. Soc. Mot. Pict. Eng.*, Vol. 42, pp. 34-57 (January 1944).

5. American Standard for Determining Residual Thiosulfate and Tetrathionate in Processed Photographic Papers, Z38.8.25-1950 (American Standards Association, 70 East Forty-fifth Street, New York 17, N. Y.).

6. American Standard for Films for Permanent Records, Z38.3.2-1945 (American Standards Association, 70 East Forty-fifth Street, New York 17, N. Y.).

PROPERTIES OF DEVELOPING AGENTS. IV. A COUPLING REACTION OF CATECHOLS

R. W. Henn and D. W. Fassett*

ABSTRACT

Many catechols and, to a lesser extent, hydroquinones and pyrogallols, couple with various *meta*-substituted phenols and anilines, including resorcinol, phloroglucinol, 1,3,5-triaminobenzene, and *m*-aminophenol to form brown-toned images consisting of an orange, red, or greenish dye accompanied by the usual black silver image. The most intense dye was produced by a combination of nordihydroguaiaretic acid and phloroglucinol.

PHLOROGLUCINOL reacts in alkaline solution with a number of phenolic developing agents to form brightly colored dyes. These dyes have been considered by the authors as a means of identification of such agents, which are important not only photographically, but as antioxidants for various purposes, including in one instance the preservation of foodstuffs. Typical hue reactions of the agents with phloroglucinol, in the presence of air, include:

Hydroquinone—orange
Nordihydroguaiaretic acid—orange
Catechol—green
Octyl hydroquinone—pale yellow
4-Phenyl catechol—orange-amber
Gentisic acid—yellow

The adsorption bands of three of these dyes are shown in Figure 1. These are for freshly prepared solutions. The saturation tends to decrease on standing.

Since the dye formation on aerial oxidation was very intense, it was thought worth while to investigate the possibility of dye formation accompanying silver development.

Experimental

The first trials were made on positive film using the combination of nordihydroguaiaretic acid and phloroglucinol, which had given a particularly intense hue in solution. Nordihydroguaiaretic acid (hereafter abbreviated as "NDGA") is a complex, naturally-occurring catechol which is used as a food preservative, and is a moderately active developing agent. Its formula is given in Table I. Phloroglucinol is symmetrically substituted trihydroxybenzene, and is not in itself a developing agent, at least under ordinary conditions. The combination in alkaline, low-sulfite developer formulas was found to yield a strongly brown image comparable to that produced by sulfide toning. When the silver of the image was bleached out with ferricyanide, a strong orange or red-orange dye image was found to remain.

The results obtained with this combination of agent and coupler were then extended by investigating a large number of developing agents and couplers. The most successful of these are reported in Tables I and II. The

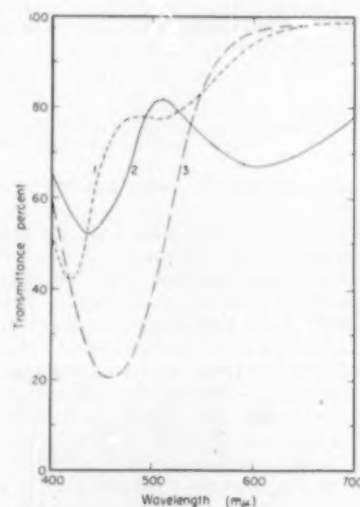


Fig. 1. Adsorption spectra obtained from alkaline solutions of phloroglucinol with (1) hydroquinone, (2) catechol, (3) nordihydroguaiaretic acid (NDGA).

data apply to Kodak Fine Grain Positive Film in a developer of the following composition:

	Molar	Grams per Liter
Developing agent	0.01	1 to 3
Coupler	0.005	0.5 to 2
Sodium sulfite	0.01	1.26
Trisodium, disodium phosphate buffer	0.2	16.4 + 14.1
Sodium hydroxide to adjust pH to 11.5		

It will be seen in reviewing Table I that no agent exceeded the NDGA in potency, although the 4-phenylcatechol was also very active, and other catechols gave some effect. In the case of the weaker agents, it was necessary to run a blank in the absence of phloroglucinol since nearly all hydroxy developing agents show some autocoupling properties at very low sulfite content and form small quantities of unsaturated dyes.

* Research Laboratories, Eastman Kodak Company, Rochester 4, New York. Communication No. 1534 from the Kodak Research Laboratories. Received 7 May 1953.

TABLE I

DEVELOPING AGENTS
(USED WITH PHLOROGLUCINOL)

No.	Name	Formula	Image (Dye + Silver)	Hue	Dye Image Intensity
1	Nordihydroguaiaretic Acid (NDGA)		Brown	Orange	Very strong
2	3,4-Dihydroxydiphenyl (4-phenylcatechol)		Red-brown	Red-Orange	Strong
3	2,3-Dihydroxydiphenyl		Warm	Purplish	Medium
4	<i>p</i> -tert-Butylcatechol		Brownish	Yellow-Orange	Medium weak
5	Catechol		Warm	Brown	Weak
6	Hydroquinone		Warm	Orange	Very weak
7	2,5-Dihydroxydiphenyl (Phenylhydroquinone)		Warm	Orange	Medium weak
8	Pyrogallol		Warm	Tan	Weak

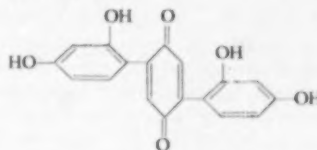
In addition to the agents entered in Table I, 4-chlorocatechol was found similar to catechol, 2,4-dichlorocatechol was somewhat stronger, and tetrachlorocatechol was quite weak. Catechols containing aldehyde and ketone groups, including protocatechuic aldehyde, 3,4-dihydroxy-*p*-acetophenone, and 3,4-dihydroxybenzophenone, failed to couple. Hydroquinones were found to be much weaker coupling agents than the corresponding catechol compounds (although they formed strong colors in solution) as were also the pyrogallols. Several orthoaminophenols were tested but, in sharp contrast to the structurally similar catechols, they failed to show any coupling reaction with phloroglucinol.

As indicated by Table II, there is probably an even wider range of couplers available for this system than developing agents. Thus, compounds containing either two- or three-*meta*-placed hydroxy or amino groups, or combinations thereof, form colors, and the hue may be varied by the nature of the substituents. In addition to the compounds listed in the table, weaker action was found for some naturally occurring polyhydroxy compounds, including tannic acid, rufigallol, and morin; *p*-nitrobenzene azoresorcinol; and for 1,3-diketohydrindene. Benzoylacetanilid, which is a coupler employed with paraphenylenediamines, coupled with the NDGA to produce a moderately dense lemon-yellow image (after the silver had been removed). Resorcyaldehyde, resacetophenone, and nitrosoresorcinol failed to couple. Neither *ortho*- or *para*-substituted dihydroxybenzenes showed any coupling action.

The conditions controlling the NDGA-phloroglucinol reaction were studied in some detail. The coupling was found to occur over the entire pH range of 10 to 13, in fairly direct ratio to the degree of silver development obtained. The dye yield decreased with increasing sulfite content, falling off sharply as the sulfite content reached the range of 0.1 to 0.2 molar. Combinations of developing agents, other than NDGA, with coupling agents, other than the phloroglucinol, were also studied. These were of some interest in extending the range of dyes available, for example, a saturated rose hue was produced by the combination of 4-phenylcatechol with chlororesorcinol, but in no case were more intense colors obtained than when the NDGA was the developing agent or phloroglucinol the coupling agent.

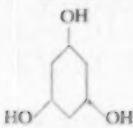
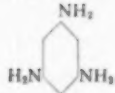

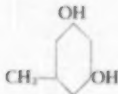
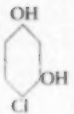

Discussion

Pummerer and Huppmann¹ have isolated a number of condensation products of quinones and phenols, including a diresorcinol quinone



which may be closely related to the dyes formed in the developing reaction, although they worked with acid

Table II
COUPLERS
(USED WITH NDGA)

No.	Name	Formula	Image (Dye + Silver)	Hue	Dye Image Intensity
1	Phloroglucinol		Brown	Orange	Very strong
2	1,3,5-Triaminobenzene		Red-brown	Red-Orange	Very strong
3	Resorcinol		Cold brown	Orange	Strong
4	Orcinol		Cold brown	Orange	Strong
5	4-Chlororesorcinol		Red-brown	Rose-Orange	Strong
6	<i>m</i> -Aminophenol		Cold brown	Orange	Strong

solution. Eegriwe² and Kesting³ mention reactions of phloroglucinol with various aromatic *ortho*- and *para*-substituted dihydroxy or aldehyde compounds in alkaline water solutions, giving rise to the formation of various orange, red, or green colors.

Practical Aspects. Most, but by no means all, of the dye-forming photographic developing reactions are obtained with the paraphenylenediamines. The systems described appear to be unreported, and are therefore worth noting, but their immediate practical value appears slight.

The brown tones produced by many of these agents (before the bleaching of the silver) brings to mind their application to monochrome work, where warm brown tones are considered highly desirable. They do appear to be reasonably applicable to the production of brown tones on positives, such as lantern slides, motion-picture film, and display transparencies. In this case, the film or lantern slide need only be exposed, developed, fixed in

a plain hypo solution, washed, and dried, as compared with the usual indirect toning processes. Unfortunately, however, toning of paper prints has proven very unsuccessful, because of the adsorption of an intense stain in the paper base, which the authors have been unable to eliminate by modifying the developer.

The dyes were found to be strongly adsorbed to textiles as well as to photographic paper, and orange-, rose-, and khaki-colored cotton fabrics were produced. However, the colors were not fast to washing in the presence of soaps or alkalis, and it would be necessary to use large molecules, to mordant the dyes, or otherwise to insolubilize them to make them practically useful.

References

1. Pummerer, R., and Huppmann, G., *Berichte*, Vol. 60: pp. 1442-1451 (1927).
2. Eegriwe, E., *Z. anal. Chem.*, Vol. 125: pp. 241-244 (1943).
3. Kesting, W., *Berichte*, Vol. 62: pp. 1422-1424 (1929).

PROPERTIES OF DEVELOPING AGENTS. V. AMINO-PHENYLPHENOLS. AN AUTOCOUPLING REACTION

R. W. Henn

ABSTRACT

The relative activities of a group of phenyl-substituted aminophenols are reported. 2-Amino-6-phenylphenol was found to produce a strong yellow-orange dye image along with the silver image, due presumably to the formation of an aminophenoxazine dye. This reaction was largely independent of the sulfite content of the developer.

THE EFFECT of phenyl substitution on the activity of aminophenol developing agents does not appear to have been previously reported. Consequently, when a group of these agents were synthesized by A. Weissberger and I. F. Salminen, of these Laboratories, a study of their relative activity was undertaken. Their activity was determined in the following formula, which had previously been employed by Armstrong, James, and Weissberger,¹ and with Kodak Motion Picture Positive Film:

Developing agent	0.01	mole per liter
Sodium sulfite	0.125	" " "
Sodium carbonate	0.15	" " "
Potassium bromide	0.0034	" " "

Wherever the hydrochloride of the developing agent was employed, a corresponding quantity of sodium hydroxide was added to neutralize the acid and maintain the pH at 10.1 to 10.2.

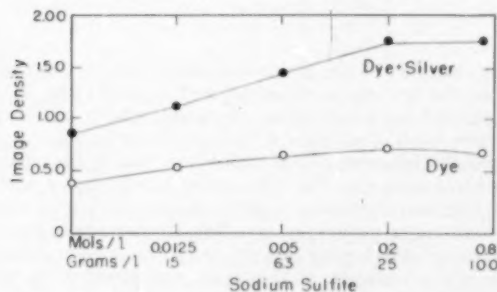


Fig. 1. Effect of sulfite content, 2-amino-6-phenyl phenol developer, at pH = 11.5. Kodak Fine Grain Positive Film. Note the high yield of dye even in the presence of high concentrations of sodium sulfite.

Table I lists the compounds which were employed and shows their relative activity. It will be seen that phenyl substitution approximately halved the activity of the *p*-aminophenol (IV vs. I) but the phenyl-substituted *o*-aminophenols (III, VI, and VII) are considerably more active than the unsubstituted *o*-aminophenol (II).

However, the interest of agent No. VI, 2-amino-6-phenylphenol, was not in its moderate activity but in the hue of the image, which was a bright sepia, not dissimilar to that produced by the sulfide toning of prints.

Treatment with ferricyanide showed this to be caused by a strong yellow-orange dye image, companion to the usual silver image. The relative strength of the dye and silver images was not markedly influenced by changes in pH, and proved remarkably unaffected by the addition of sulfite. This is indicated in Figure 1, where the silver and dye image densities, read on a photoelectric densitometer with a fairly high blue response (Photovolt), are plotted against the sulfite content.

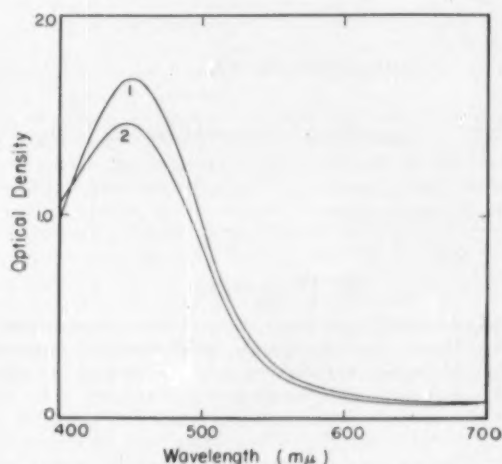


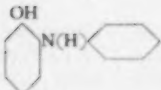
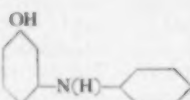
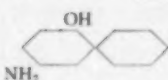
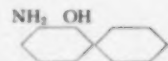
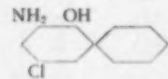


Fig. 2. Dye adsorption curves of (1) the auto-coupling 2-amino-6-phenylphenol developer, and (2) 4-amino-N,N-diethylaniline plus acetoacetanilid, at pH = 11.5. Kodak Fine Grain Positive Film. The aminophenol was employed with 0.2 molar sodium sulfite, the paraphenylenediamine, with 0.02 molar sulfite.

It is of interest to compare this autocoupling developer with the well-known paraphenylenediamine coupling developers. Figure 2 shows the adsorption curves of the dyes obtained from (1) the 2-amino-6-phenylphenol, and (2) a mixture of 4-aminodiethyl aniline (as the developer) and acetoacetanilide (as the coupler). The similarity is evident. The stability of the two dyes towards ultraviolet radiation was also similar. However, the aminophenol produced rather more dye relative to the silver image than did the paraphenylenediamine.

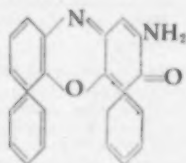
Table I
AGENTS TESTED AND RELATIVE ACTIVITY
(pH = 10.0; KODAK MOTION PICTURE POSITIVE FILM)

No.	Name	Formula	Relative Activity		Image Hue
			Time, D ₁ = 2.0 (Min.)	T ₁ /T	
I	<i>p</i> -Aminophenol		3.0 (T.)	1.00	Black
II	<i>o</i> -Aminophenol		55.0	0.055	Warm black
III	2-Hydroxydiphenylamine		11.0	0.27	Black
IV	3-Hydroxydiphenylamine		No Development		...
V	4-Amino-2-phenylphenol		6.3	0.47	Black
VI	2-Amino-6-phenylphenol		5.0	0.60*	Sepia
VII	2-Amino-4-chloro-6-phenylphenol		5.2	0.57*	Black

* Incompletely soluble.

Discussion

Fischer and Jonas² have shown that *o*-aminophenols on oxidation, as, for example, with mercuric chloride, form aminophenoxazone dyes. In the case of the agent under discussion, this would be:



It is obvious that substitution in the positions 5 or 6- to the phenyl grouping would interfere with the coupling reaction, which explains the lack of dye formation when employing agent VII.

The interest of the present example lies in the intensity of the dye image obtained, and its formation in the presence of large quantities of sulfite, which ordinarily interfere with coupling reactions. The sepia hue, given by the combination of dye and silver (before bleaching) may be of some interest in pictorial photography, but is rather yellower than is usually desired, and some stain is produced on paper prints. The further addition of a competing developing agent, such as hydroquinone, reduces the intensity of this stain and produces brown-black images.

References

1. Armstrong, E. C., James, T. H., and Weissberger, A., J. Amer. Chem. Soc., Vol. 63, pp. 182-185, 1941.
2. Fischer, O., and Jonas, O., Berichte, Vol. 27, p. 2782, 1894.

METHODS FOR ELIMINATING THE IMAGE ON ONE SIDE OF DOUBLE-COATED X-RAY FILM

H. F. Sherwood*

IN SOME scientific applications of x-ray film, such as x-ray diffraction studies, autoradiography, and micro-radiography, it may be necessary to avoid the parallax associated with the presence of two images on opposite sides of the base. To obtain single-coated films which are suitable for a particular experiment involves special manufacturing procedures and usually involves some delay. Commercial double-coated x-ray films, on the other hand, are readily available and are particularly designed to respond to x-rays. The use of simple methods which can be applied by the experimenter himself to utilize one emulsion only would certainly expedite his work. The methods described in this note are not necessarily new—a chemical method has been described by Stevens,¹ but some of the details warrant discussion.

Two general procedures have been tested: (1) the unwanted emulsion may be removed chemically after processing, or (2) it may be covered with some waterproof sheet material prior to development, after which the sheet is removed for normal fixing. Several Kodak x-ray films were used in these tests and were processed in the conventional manner. Except for the specific test in which films taped to the bottom of the developing tray were investigated, they were developed in a deep tank as commonly used in x-ray darkrooms.

Chemical Removal of Emulsion

The unwanted emulsion can be removed from the developed, fixed, washed, and dried film by the following method: The film is placed on a sheet of glass and its edges are taped down with the wanted emulsion against the glass. A one-half normal solution of potassium hydroxide (28 grams of potassium hydroxide per liter of water) is applied to the emulsion which is to be removed, with a swab of cotton or a soft brush and left until the gelatin has softened. Usually a few minutes are adequate. The emulsion is then brushed off with a stiff brush, such as a toothbrush, and the remaining loose particles are rinsed off with tap water. After removal of the undesired emulsion, the film should be placed in x-ray acid fixing bath to neutralize any remaining caustic. It is then washed for 20 minutes and dried, but a shorter washing time is satisfactory if the films are not to be kept indefinitely. The only advantage of this method is that it permits examination of the double-emulsion image before one is removed—a feature which is probably rarely needed. Protecting the wanted emulsion from the caustic solution requires considerable care in applying the tape to be sure that there are no wrinkles where the liquid can leak through. Rubber gloves and an apron should be worn by the operator to protect his skin and clothing.

* Research Laboratories, Eastman Kodak Company, Rochester 4, New York. Received 27 August 1953.

Waterproof Covering of Emulsion

If a single strip of tape is wide enough to cover the area to be protected, the desired emulsion may be covered with waterproof adhesive tape. This may be particularly applicable to narrow diffraction films. It is not advisable to overlap several strips of tape to compensate for the narrow width of the tape, because the adhesive coating of the tape does not always adhere well enough to the back of the adjoining layer to prevent leakage.

When tank processing is employed and x-ray sheet-film hangers are used, it is possible to process two films of equal size simultaneously. This may be done by placing the two unwanted emulsions in contact and binding the edges of the film tightly together with adhesive tape in the same fashion as lantern slides are bound. An alternative method for large numbers of small films is to tape them to a large sheet of film base or to a discarded radiograph. One 14- by 17-inch sheet affords adequate space on each side for two 8- by 10-inch films. Films mounted in this manner should, if possible, be taped down independently of each other, because it was found that when the edges of two films were butted together and fastened down with a single strip of tape, leaks frequently occurred.

If the image extends to the very edge of a film, it will be partially cut off if the tape extends over the edge on both sides. In order to retain this part of the image, the protective cover should be cut smaller than the film, leaving a border, say $\frac{1}{4}$ inch wide, all around. The tape is then applied to the border and extends onto the cover about the same amount, leaving the opposite side of the film entirely free of tape. The mounted film may then be fastened in a suitable hanger and processed.

When tray processing is used for a single film, it can be taped directly to the bottom of the processing tray and the desired emulsion completely processed before removing the tape for clearing of the undesired emulsion; or, after the stop bath has been removed from the tray, and before the fixer is added, the tape may be removed and both emulsions allowed to fix at the same time.

The following are examples of tapes which were found to give sufficiently watertight joints: Scotch Brand Plastic Electrical Tape No. 22, Mystik Self-Stik Masking Tape (paper), Bayhesive Adhesive Plaster (cloth), and Johnson and Johnson Waterproof Adhesive Tape (cloth).

Precautions

The principal cause of leakage of solution to the protected emulsion is the small opening which may exist along the line where the tape fails to make contact between the edge of the film and the supporting surface. A fingernail or some blunt instrument should be run along all edges to close the space as effectively as possible.

Capillary action and hydrostatic pressure must both contribute to the tendency of solutions to enter wherever

the tape contact is not perfect. The effect of hydrostatic pressure will be minimized if tray processing is used rather than deep-tank processing, but the latter has proved feasible if sufficient care was taken with tape contact.

Because joints are the principal source of leaks, overlapping of several tapes to make up for insufficient width of one is not recommended. The number of joints should be kept to a minimum.

The tape used should be reasonably fresh so that it will adhere well. It should never be re-used.

The white lights in the darkroom should not be turned on until the unwanted emulsion has cleared.

References

1. G. W. W. Stevens, "The Removal of an Unwanted Image Layer from One Side of Double-Coated X-ray Film Negatives," *J. Scientific Instruments*, Vol. 20, pp. 133-134 (1943).

THE USE OF PHOTOGRAPHY IN DETECTING AND PROVING VOTE FRAUDS

JOSEPH THOLL*

PHOTOGRAPHY as an analytical, comparative tool can be effectively used for the demonstration of many limited forms of legal evidence. The more circumscribed the evidence, the greater the need for a clear, graphic exposition since vital facts may appear relatively insignificant and unimportant in their original state. Where a single symbol like an "X" mark is under scrutiny the utilization of sufficiently enlarged macro-photographs is essential both for examination and demonstration. In an Ohio vote fraud investigation such photographs brought out the fine details of pencil marks and were used, first, in the laboratory and later assembled on charts for courtroom demonstration. Through applied photographic techniques it became practical to record, analyze, organize and consolidate a huge mass of material and to present it before the Court in a logical, comprehensive and convincing manner.

In an investigation started in the autumn of 1952 by Ohio Secretary of State Ted W. Brown more than 250,000 ballots cast in the Cuyahoga County (Cleveland area), Primary elections were examined for evidences of fraud. After completing the initial phases of the Cuyahoga probe (which served as a model for other investigations) in which the ballots were screened, a careful, methodical examination was commenced with two objectives, namely: (1) to detect evidence of fraudulent voting (short penciling)[†] where it was apparent that a ballot was filled in by more than one hand; (2) to identify, if possible, the hand which inserted the fraudulent marks. The suspects in each precinct were limited to the six officials representing each party and the ballots in each case were limited to a legal maximum of three hundred.

Although photography was not employed during the early screening of the ballots it was considered indispensable later on to record each progressive stage in the uncovering of fraud from the first detection of fraudulent marks to the identification of their maker. In the heat of trial these chronologically related photographs proved

to be the very backbone of the Prosecutor's case. Also it was evident from the very first contest that great reliance would have to be placed, in pending cases, upon demonstrative charts through which the jury could be made to analyze, compare and identify the evidence as well as to substantiate the findings of various expert handwriting witnesses.

In addition to the photographic charts, an opaque projector taking copy up to 11 by 11 inches was used to project both original matter and photographs on a seventy-inch screen. The greatly enlarged images on the screen helped to bring out significant aspects in the exhibits that were retained by the charts in the jury room.

The Fraud "Pattern"

The illegal votes for candidates neglected by the legal voters were detected where a ballot contained "X" marks which appeared to have been made by more than one hand. There were actually a few cases where the vote thieves used ink (Figure 2) to mark votes for candidates in blank spaces left by the legal voter who, of course, had used a regulation pencil in voting. In one instance a number of different ballots were altered with the same red pencil. Occasionally from one to as many as seventeen candidates were invalidated by the addition of one illegal vote which caused all the legal votes to be thrown out. Many of the fraudulent "X's" cancelling out the legal votes were so unlike the legal voter's marks that the differences could be readily discerned on the ballot itself. The discovery of traces of illegal voting, however, was but a preliminary step towards the tracking down and identification of the "short pencil" artists.

Once a series of suspicious "X" marks was located it was determined, whether or not, such markings appeared consistently before certain candidates. In each locality investigated a particular coterie of candidates was found to have been marked in by the illegal operators. In some precincts the candidate for Central Committeeman (a local political office) marked himself in on a number of ballots. Where a combination of candidates was consistently "short penciled" with the same characteristic design of "X" mark, which differed

* Examiner of Questioned Documents, 58 Bellview Avenue, Chagrin Falls, Ohio. Received 27 August 1953.

[†] The term "short penciling" originally referred to the practice of concealing a short length of pencil in the palm of the hand, or a short piece of graphite under a finger nail, to be used illegally in a voting booth or during the opening and counting of ballots. The term is now used to cover any form of fraudulent marking of ballots.

from other genuine cross marks on the ballot, a "pattern" was established and the presence of fraud determined. It was thus possible to determine which marks on a ballot were placed by the legal voter and which ones were inserted after the polls closed.

The finding of suspicious markings did not necessarily provide evidence of fraud. If the questionable "X's" were few in number and did not follow the form of a "pattern" they were eliminated from consideration despite their variance with other "X's" on the ballot.

The proper recording of each series of questioned marks making up a "pattern" constituted a vital link in the preparation of the States' case for it was the function of applied photographic techniques to preserve and convey the full impact of such incriminating evidence to the Court and jury. The technical data and procedures employed in this investigation are discussed below.

Comparison and Identification

The comparison and identification of questioned and specimen "X" marks was based on the consideration of over fifty possible points of common similarity. A combination of from six to twenty of these was held sufficient for an identification, depending on their probability of use. These fifty odd points of identification were consolidated, for purposes of testimony, into twelve general classifications as follows: (1) Writing implement. (2) Design (Latin cross, Greek cross, or "X" mark). (3) Degree of skill. (4) Tempo of execution. (5) Initial and final formations at the extremities of strokes. (6) Proportions of strokes. (7) Sequence of

Fig. 2. Specimen "X's" (left) submitted by a defendant consist of "Latin cross" and "X" designs. Fraudulent votes from three questioned ballots (right), made with black ink, contain the same unusual combination of styles.



strokes and location of thick and thin strokes. (8) Pressure. (9) Size. Vertical and horizontal alignment within the printed enclosure. (10) Comparative size of angles. (11) Degree of curve or straightness of lines. (12) Nature and extent of variation.

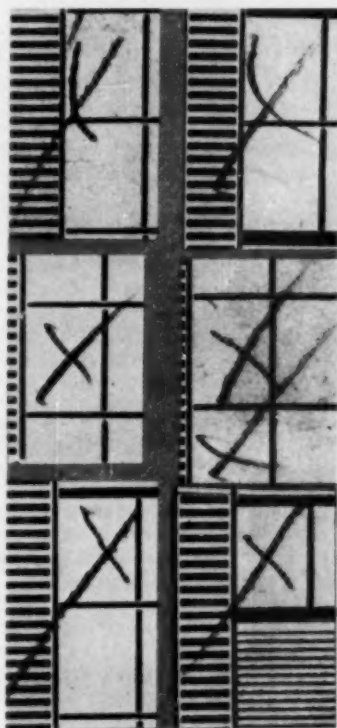
The identification in each case was not based merely on common similarity but on a unique combination and a sufficient number of coincidental points. The great numbers of questioned and standard (genuine) "X's" compensated for the restricted nature of this type of evidence.

Once an identification was made, photographic charts were constructed through which each point of common similarity was brought out and emphasized by means of enlargement and a juxtaposed arrangement of coincidental writing habits (Figure 3). These charts which were self-explanatory made it possible for the jury to evaluate the evidence independently of the expert handwriting witnesses and served to counteract unfounded, diverting attacks by the defense. Also, questioned marks and corresponding genuine marks from suspects were photographed under ruled squares, a device which facilitates comparison of similar or identical portions of writing. (Figure 4).

Individual Combinations of "X" Marks

Still another condition was used as the basis for the identification of questioned "X" mark patterns. It was observed from specimens submitted by suspects that as many as five styles of "X" marks were habitually used by a single individual (Figures 1, 2). In most cases this combination of styles was nothing more than characteristic variation, but, there were a few instances

Fig. 1. Standard "X" marks (left) from a defendant's own ballot are compared with fraudulent "X's" from three different tampered ballots. The fraudulent "X's" were obviously different from other marks on the three questioned ballots whereas the defendant's "X's" were uniform throughout his own ballot. Note combination of three distinct but related styles of X's.



where "X's" were quite dissimilar (Figures 1 and 2). This unique combination of styles, either similar or dissimilar, proved to be a valuable, indispensable factor in the identification of questioned "patterns."

For example, a series of fraudulent marks was found to consist of three distinct styles (Figure 1) which corresponded with three identical styles on the suspects own ballot. The problem of proving that this triple combination of "X's" was produced by one hand was achieved by a photographic chart on which the dissimilar questioned marks were matched with the suspect's marks. This combination of "X's" when viewed individually on scattered ballots tended towards confusion and indecision whereas the entire group of marks when viewed simultaneously in an enlarged, classified and juxtaposed set-up left little doubt as to their common origin. During the trial the defense lawyers were unable, despite much searching, to find another voter in the precinct who duplicated these three "X" mark designs.

Finding the Suspects Ballots

Inasmuch as many of the suspected officials either disguised their "X's" or refused to submit specimens it became necessary to locate their actual voted ballot which contained undisguised "X" marks made under more favorable conditions. This ballot, filled out and cast by the suspect, was traced by first finding his assigned voting number listed in a Poll List book and then locating an identically numbered stub kept with other stubs in a separate, labelled bag. By matching the tears and perforations on the stub with corresponding ones on one of the precinct ballots it was possible to show that these two portions originally comprised the entire, untorn ballot assigned to the suspect. This ballot then, in addition to voluntarily submitted specimens, became the standard of comparison with questioned "X" mark patterns.

These two matching torn sections were carefully fitted together under the weight of a six inch wide strip of glass and photographed. When enlarged two diameters the identical matching of the stub and ballot was quite

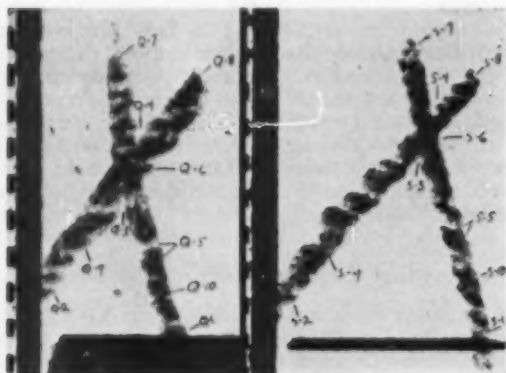


Fig. 3. Common points of similarity between a questioned "X" and an "X" of known authorship marked on 20 diameter enlargements of the photographic records for demonstration to the Court.



Fig. 5. Enlarged section of a ballot stub matched with a torn-off ballot to establish identification of a defendant's own legal ballot for handwriting comparison purposes.

apparent. A five diameter enlargement of the fitted sections showed interlocking serrations which could not be easily seen by the unaided eye. (Figure 5).

The legitimate voted ballot of the suspect was traced and used even where specimen "X" marks were submitted because, invariably, a guilty booth official attempted to disguise his specimen "X" marks, a relatively easy thing to do. This subterfuge was revealed when the disguised and bona fide "X's" were compared. Had it not been for this system of finding the suspect's voted ballot this investigation would have been terminated ingloriously in its very early stages. With the aid of such ballots, as standards of comparison, every suspect identified was indicted by the Grand Jury.

Court Procedure

In the vote fraud investigation the bulk of the State's cases was made up largely of "X" marks because the taciturnity of witnesses and defendants alike brought forth little in the way of supporting evidences. The burden of proof therefore fell upon expert handwriting witnesses who relied on applied photographic techniques to show fraud and establish identity with circumstantial evidence.

The following order of court presentation was worked out so that each progressive phase of the examination could be most advantageously demonstrated, from the detection of questioned "X's" to the establishment of a "pattern," and finally to the identification of the already indicted defendant.

1. Illegally marked ballots were displayed to the jury in their original form and projected on the screen to show the "crime." Nothing was said at this point with reference to identification.

2. A distinction was made between the *superficial or natural differences which occur as variation in an individual writing and the fundamental differences which distinguishes the handwriting of various persons*. These two classes of "differences" were illustrated by composite photographs and with specially arranged, folded ballots in the opaque projector. This discussion was found necessary to counteract the stock argument of the defense that any difference, however trivial, rendered identification by comparison, void.

3. The basis of identification was discussed with reference to the singular combination and number of identifying characteristics and styles comprising the pattern in question.

4. At this stage of the trial it was necessary to introduce standard (genuine) specimens of the defendant's "X" marks so that they could legally be used for comparison with the questioned "pattern." For this purpose an enlarged photograph of the matching torn sections of the defendant's numbered stub and corresponding ballot were submitted to the Court. The defendant's voluntary specimens were also entered into the evidence.

5. The comparison between the questioned "pattern" and the defendant's "X" marks comprised the final phase of the expert testimony. The unique combination of characteristics and styles was now compared with the same features appearing in the defendant's own "X's." This demonstration was made first, with the ballots themselves, then with photographs enlarged up to twenty diameters, and finally with composite photographs in the opaque projector.

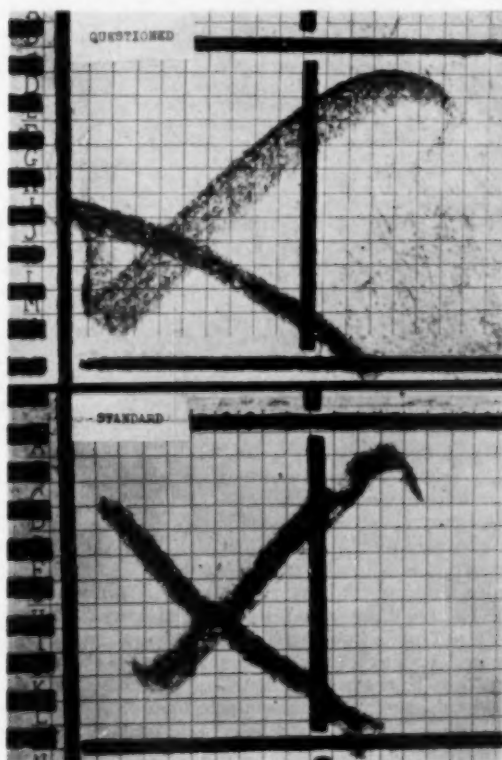


Fig. 4. Comparison of a questioned mark with an identified mark photographed with superimposed ruled squares. The questioned mark had been hastily made whereas the identified mark had been executed with greater deliberation but the similarities are apparent.

Photographic Technique

The applied photographic techniques utilized in recording and consolidating the evidence of voting frauds and the preparation of analytical charts were adapted to the special needs and circumstances of these cases. One difficulty was the lack of ideal working conditions in an improvised darkroom from which the impounded ballots could not be moved until time for trial. Once negatives were made it was possible to complete the printing and mounting in the photographer's own darkroom.

Equipment. An 8 × 10 view camera with a 5 × 7 reducing back arranged in a vertical copying position on a tripod was found practical for the limited space available. The lens was a 7 inch focal length anastigmat and the dividing back permitted two separate exposures on each 5 × 7 film.

Lighting. A single 500-watt photoflood lamp was placed at the side of the copy at an approximate angle of forty five degrees to emphasize textural details. The relative position of the light source and copy was standardized as much as possible for uniformity of lighting and exposure.

Film and Processing. Since much of the evidence was made up of faint and worn (from handling) pencil marks use was made of litho-type films such as Reprolith and Kodalith in conjunction with a 75 per cent normal development in D-72 diluted one to three. This technique* reduces the high inherent contrast of the film while increasing the tonal gradations. Litho films, with modified processing, record paper surfaces and faint pencil impressions in a manner similar to reflected ultraviolet photography (Figure 5). This film because it is fine grained and quickly processed was admirably suited to the difficult working conditions and great volume of copying encountered in the vote fraud investigations.

Copying Procedure. The "X" marks were photographed separately on a split half of 5 × 7 film at a direct ground glass enlargement from two to three diameters. Each mark was focussed critically through a clear section of ground glass with a focusing device and was identified with a small coded strip of paper containing essential data. The exposure of 10 seconds at an aperture of f/11 was timed to bring out shadow detail.

Printing and Mounting. Once the negatives were dried they were removed to the photographic darkroom where both contact and projection prints were made. In most cases the negatives were enlarged seven times giving a total enlargement of about twenty diameters. The enlarger was a specially built horizontal type. The light and negative characteristics made the use of chloride paper practical. After completion the prints were trimmed, classified, arranged and finally mounted on black poster board.

* See "Uses of Kodalith Film in the Examination of Questioned Documents", PHOTOGRAPHIC SCIENCE AND TECHNIQUE, Oct. 1952, pages 96-99.

MECHANISM OF SUPERADDITIVITY IN PHOTOGRAPHIC DEVELOPMENT

T. H. James*

ABSTRACT

Superadditivity can be produced by regeneration of an oxidized developing agent only under certain conditions, and regeneration is not a general cause of superadditivity. An experimental study is made of superadditivity in the following combinations: Metol-hydroquinone, Metol-hydroquinone monosulfonate, 1-phenyl-3-pyrazolidone-hydroquinone monosulfonate, 1-phenyl-3-pyrazolidone-*d*-arabascorbic acid, diaminodurene-hydroquinone monosulfonate, and Metol-*d*-arabascorbic acid. The superadditivity of the Metol-*d*-arabascorbic acid mixture can be explained on the regeneration theory, but the detailed mechanism involves removal of or prevention of formation of an inhibiting oxidation product. The superadditivity of the pyrazolidone combinations cannot be explained by a regeneration mechanism, but can be explained on the basis of (1) initiation of development by the pyrazolidone, with resulting decrease in the charge barrier, and (2) formation of a quaternary ion oxidation product, with further decrease in the charge barrier. The superadditivity of the other mixtures probably involves these same factors. It is shown that in all of these combinations the formation of a quaternary ion of activity equal to dodecyl pyridinium ion would suffice or more than suffice to account for the superadditivity of the combination.

THE SUPERADDITIVITY of the Metol-hydroquinone developer combination has received considerable experimental and theoretical attention in the past, but it does not appear that any of the explanations which have been offered can account completely for the phenomenon. Prior work on superadditivity was reviewed recently by Levenson,¹ who proposed a new mechanism. Levenson suggested that superadditivity can occur in a complex developer when the reduced form of one of the developing agents, A, can readily reduce silver bromide and the other developing agent, B, can reduce the oxidized form of the first.

Some further discussion of Levenson's mechanism seems desirable to indicate the possible ways in which it could account for a superadditive effect in development. There are several such ways. (1) Developer B, which, by itself, develops more slowly than A, may act in the combination primarily to increase the effective concentration of A in the vicinity of the developing grains. (2) In the reduction of the oxidized form of A, an intermediate may form which is more active than the original developer. (3) If an oxidation product of A inhibits development, regeneration may be effective primarily because of removal of the inhibiting agent.

In considering the first alternative, we can choose two extreme cases. If diffusion of the developing agent from the solution to the reaction sites is rapid in comparison

with the rate of the chemical reaction, no significant increase in concentration of agent A can be effected by regeneration, since diffusion will maintain the original concentration. If diffusion is slow in comparison with the chemical reaction, the rate of development will be largely determined by the rate of diffusion. If developing agent B reacts very rapidly with oxidation product of A to regenerate it, and if the rate of diffusion of the two developing agents is the same, the effective concentration of A at the reaction site will be increased by the presence of B, and superadditivity will occur.

The second alternative, regeneration of an active intermediate, cannot be definitely eliminated on the basis of our present knowledge, but it appears unlikely in the Metol-hydroquinone combination. The active intermediate would be the semiquinone of Metol. There is no evidence to indicate whether this semiquinone is more active than the fully reduced form. However, LuValle² has shown that in the oxidation of hydroquinone in the presence of sulfite, the sulfite reacts rapidly with the semiquinone, with eventual formation of the sulfonate, and oxidation to the quinone form does not occur. It seems probable that the situation is the same in the Metol-sulfite solutions.

The third possibility presupposes the formation of an inhibiting oxidation product in the reaction of the first developer. Many examples of such inhibiting oxidation products are known. Striking examples have been found^{3,4} among the derivatives of *p*-phenylenediamine. A marked increase in the rate of development by such developers can be obtained by adding either sulfite or couplers which react rapidly with the offending oxidation product, or perhaps prevent its formation by reacting with some intermediate. A reducing agent

* Eastman Kodak Company, Rochester 4, New York. Communication No. 1598 from the Kodak Research Laboratories. Received 17 August 1953. A shorter version of this paper has been presented at the Royal Photographic Society Centenary International Conference of the Science and Applications of Photography, in London, in September 1953, and will be published with the other conference papers.

which would rapidly reduce the oxidized form of the developer should accomplish the same purpose. To produce superadditivity in the presence of sulfite, however, the reducing agent would have to be more effective than the sulfite in eliminating the inhibiting oxidation product.

It is clear that the regeneration mechanism offers several possibilities of accounting for superadditivity in complex developers. However, some experimental evidence obtained by the writer made it appear unlikely that any of these possibilities can account completely for the superadditivity of the Metol-hydroquinone developers. Moreover, evidence obtained in a study of the strongly superadditive combination of 1-phenyl-3-pyrazolidone and hydroquinone monosulfonate indicates that, although regeneration occurs, another mechanism is primarily responsible for the superadditivity.

Experimental

The photographic materials used in this investigation were Eastman Release Positive Film and Eastman High Contrast Positive Film. The developer solutions were made up in two parts: (1) The developing agent or agents were dissolved in 200 cc. of 0.002 M hydrochloric

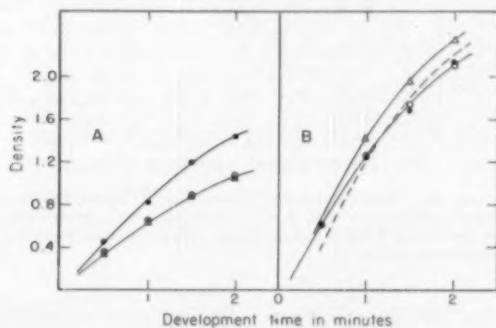


Fig. 1. Development by Metol combinations of Eastman Release Positive Film. A. No sulfite, 0.0067 M KBr, pH 8.7, Log E 1.90: ○ ○ 0.025 M Metol; Δ Δ 0.025 M Metol + 0.05 M hydroquinone; ● ● 0.025 M Metol + 0.0067 M *d*-araboascorbic acid. B. 0.05 M Na₂SO₃, otherwise as A: ---- Film pretreated in 0.001 M dodecyl pyridinium salt, then developed in hydroquinone containing dodecyl pyridinium salt.

acid, and (2) the buffer and other addenda were contained in 100 cc. of water. The two solutions were deaerated separately by passing Linde High-Purity nitrogen through them in an apparatus previously described,³ and they were mixed in this apparatus to form the developer solution proper. Burst nitrogen agitation was used throughout during development of the film, and all operations were carried out at 20.2 C. The film was exposed on the Eastman IIB Sensitometer, using the standard positive light source and filter.

Metol-Hydroquinone Mixtures

Experiments were carried out with mixtures of Metol and hydroquinone and of Metol and *d*-araboascorbic acid, both with and without sulfite, at pH 8.7 and in the presence of 0.0067 M potassium bromide. Some results

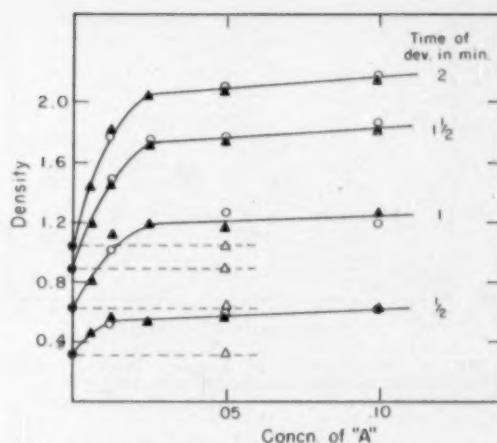


Fig. 2. Effect of *d*-araboascorbic acid and sulfite on development by Metol. Conditions same as for Fig. 1. "A" = Na₂SO₃ (○ ○), *d*-araboascorbic acid (▲ ▲), hydroquinone (△ △).

are illustrated in Figures 1 and 2. Figure 1A gives the density-time curves for log E = 1.9 exposure and development in Metol plus hydroquinone, Metol plus *d*-araboascorbic acid, and Metol alone, all in the absence of sulfite. The curves for Metol alone and for Metol plus hydroquinone coincide, showing that the hydroquinone has not increased the activity of the developer. The curve for the Metol plus ascorbic acid lies definitely above the other two, however, showing that the ascorbic acid has increased the activity of the developer. Development by the ascorbic acid alone at this pH is extremely slow.

Figure 1B shows the results of similar experiments carried out in the presence of 0.05 M sodium sulfite. Under these conditions, the curves for the Metol alone and for the Metol plus ascorbic acid coincide, whereas the Metol-hydroquinone mixture shows definitely higher activity. Hydroquinone by itself develops very slowly in the presence of sulfite at pH 8.7. However, this low activity can be attributed largely to the charge-barrier effect,^{3,6} and when this effect is minimized, the hydroquinone is nearly as active as the Metol. The broken curve in Figure 1B represents development of film pre-bathed in 0.001 M lauryl pyridinium *p*-toluenesulfonate to minimize the charge effect, and then developed in a solution of hydroquinone plus the quaternary salt.

Figure 2 shows the dependence of the activity of Metol solutions on the presence of various quantities of sodium sulfite, hydroquinone, and *d*-araboascorbic acid at pH 8.7. It is seen that both sodium sulfite and the ascorbic acid increase the rate of development. The major increase, however, is brought about by concentrations of 0.025 M or less. At higher concentrations, the rate of development is nearly independent of concentration of sulfite or ascorbic acid, and the two compounds are of equal effectiveness. Hydroquinone is ineffective. These experiments show that, in the absence of sulfite, the ascorbic acid is increasing the rate of development by the Metol by removing or preventing the formation of inhibiting oxidation products.

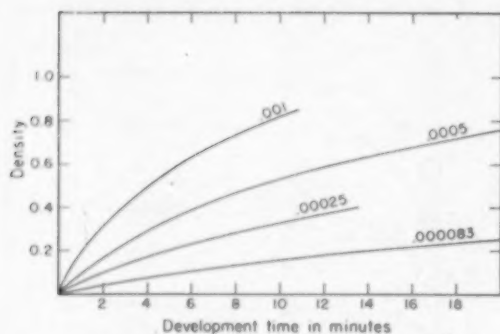


Fig. 3. Development of Eastman High Contrast Positive Film by Phenidone at pH 9.5. Log $E = 1.75$. Numbers on curves are developer concentrations.

The experiments of Weissberger, Thomas, and Lu-Valle⁶ show that *D*-araboascorbic acid and *L*-ascorbic acid are very effective inhibitors of the autoxidation of Metol. The inhibitor acts to regenerate the Metol by reducing the semiquinone, and thus prevents quinone catalysis. Metol-ascorbic acid developers of pH 9-10 can be prepared which will remain colorless for several days on exposure to air in open flasks. The superadditivity of the Metol-ascorbic acid combination is an example of a regeneration mechanism of the third type discussed previously. The superadditive effect is not observed in the presence of sulfite because the sulfite is as effective as the ascorbic acid in preventing the accumulation of inhibiting oxidation product.

It does not appear from the preceding experiments that hydroquinone is sufficiently active as a reducer of oxidized Metol to prevent the formation of the inhibiting oxidation product. In the absence of sulfite, the hydroquinone failed to increase the rate of development in the Metol-hydroquinone solution. In the presence of sulfite, which prevents the formation of the inhibitor, however, some superadditivity is noted. It does not appear that this can be explained by assuming that the hydroquinone is much more effective as a regenerating agent in the presence of sulfite, since the experiments with the ascorbic acid indicate that under the prevailing conditions, regeneration by reduction of oxidation product is no more effective than removal of oxidation product by reaction with sulfite. Evidently another explanation must be found.

1-Phenyl-3-pyrazolidone-Hydroquinone Monosulfonate Mixtures

A developing agent disclosed by Kendall^{7,8} gives a highly effective superadditive mixture with hydroquinone. In general, considerably smaller amounts of this agent, 1-phenyl-3-pyrazolidone (Phenidone), than of Metol are required to give an equal degree of superadditivity. Phenidone gives an even higher degree of superadditivity with hydroquinone monosulfonate than with hydroquinone, and the monosulfonate mixture was chosen for the present study.

A series of experiments was carried out in which the concentration of sodium hydroquinone monosulfonate was kept constant at 0.005 M and the concentration of

Phenidone was varied. The solutions were used without addition of sulfite or bromide, and were buffered at pH 9.42 with sodium metaborate. The rates of development by Phenidone are indicated by the density-time plots shown in Figure 3. Development occurs without induction period at all concentrations. The rate of development by the hydroquinone monosulfonate used alone is much slower. The densities obtained at 20, 40, 70, 150, 180, and 200 minutes were 0, 0.04, 0.10, 0.20, 0.25, and 0.30, respectively.

The development curves obtained with the combination of the two developing agents are given in Figure 4. A significant feature of these curves is the presence of a marked induction period in the curves representing the lowest Phenidone concentration (0.00083 M) and the decrease of the relative induction period as the concentra-

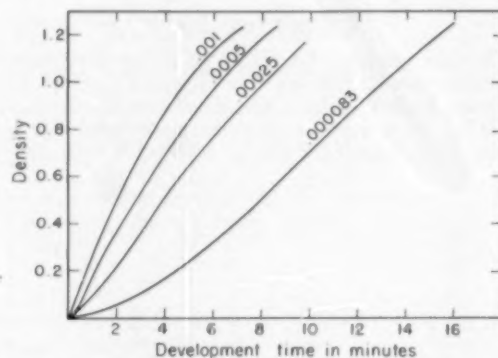


Fig. 4. Development by Phenidone + hydroquinone monosulfonate at pH 9.42. Numbers on curves refer to the Phenidone concentration. Hydroquinone monosulfonate, 0.005 M.

tion of Phenidone increases. Figure 5 gives a measure of the extent of the superadditivity. The solid curves were obtained by subtracting for each development time the density obtained with Phenidone alone (from Figure 3) from the density obtained with the combination (from Figure 4). Since the hydroquinone monosulfonate by itself produces no density within the time considered, the resultant curves represent the superadditivity in terms of time. If superadditivity is considered in terms of rate of development at a given density, the solid curves of Figure 5 should be corrected for development by the hydroquinone monosulfonate alone, but this correction amounts at most of 0.005 density unit per minute, and so is insignificant.

The broken curve in Figure 5 represents the development obtained in the absence of Phenidone with a solution of 0.005 M sodium hydroquinone monosulfonate and 0.001 M dodecyl pyridinium *p*-toluenesulfonate at pH 9.42. It is evident from this curve that the hydroquinone monosulfonate itself is a fairly active developer when the charge effect is minimized by the use of a quaternary salt. The activity is, in fact, more than would be necessary to account for the superadditivity of the Phenidone-hydroquinone monosulfonate mixture if the Phenidone in some way could minimize the charge effect.

1-Phenyl-3-pyrazolidone-*d*-Araboascorbic Acid Mixtures

Phenidone and *d*-araboascorbic acid form an effective superadditive mixture. Figure 6 shows the development curves obtained with 0.0005 M Phenidone and with a mixture of 0.0005 M Phenidone and 0.005 M ascorbic acid at various pH values. In the construction of this figure, the time scale for each pH has been adjusted so that the curves representing development by Phenidone alone coincide (Curve 1). Curves 2, 3, 4, and 5 represent the Phenidone-ascorbic acid mixtures at pH 6.3, 7.6, 8.9, and 10.5, respectively. It is evident that the superadditive effect increases with increasing pH. Furthermore, development by the mixture starts at the same rate as development by Phenidone alone, then subsequently increases, and may reach as much as five times the initial rate.

The shape of the development curves obtained with the mixture argues strongly against a regeneration mechanism of superadditivity in these developers. The maximum rate of development by Phenidone occurs at the very start of the process. The rate of development by the mixture is the same at the start of the process, but then starts to increase after an initial developed density has been built up. Simple regeneration of Phenidone could not bring about this kinetic effect. The same argument can be applied to the results with the hydroquinone monosulfonate. At low initial concentrations of Phenidone, the lower part of the density curve bends upward from the time axis. The rate of development continues to increase until a density of 0.2 to 0.3 is obtained, at which time the rate is several times greater than the initial rate.

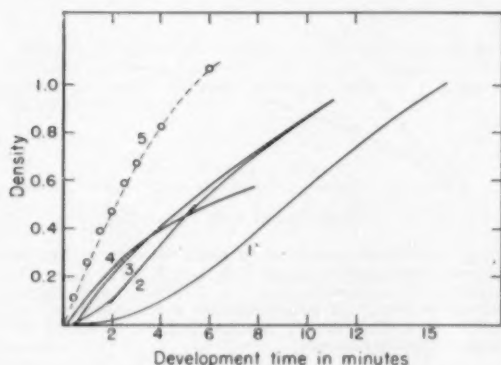


Fig. 5. Superadditive effect for Phenidone + hydroquinone monosulfonate combinations for Phenidone concentrations of: 1, 0.000083 M; 2, 0.00025 M; 3, 0.0005 M; 4, 0.0010 M. ---- Development by 0.005 M hydroquinone monosulfate + 0.001 M dodecyl pyridinium *p*-toluenesulfonate.

Although regeneration does not account for the superadditive properties of the mixtures of Phenidone with hydroquinone, hydroquinone monosulfonate, and *d*-araboascorbic acid, some regeneration evidently does occur and is of importance to the practical properties of the developers. An alkaline solution of Phenidone quickly becomes discolored in air, the coloration ranging

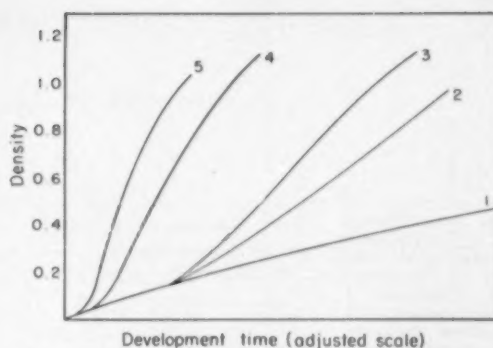


Fig. 6. Effect of pH on superadditivity of Phenidone + *d*-araboascorbic acid mixtures. Curve 1, Phenidone alone; 2, mixture at pH 6.3; 3, mixture, pH 7.6; 4, mixture, pH 8.9; 5, mixture, pH 10.5.

from yellow-orange to green, depending on pH. The discoloration does not occur in the presence of the ascorbic acid. The solution likewise remains colorless if hydroquinone, hydroquinone monosulfonate, Metol, and certain other developing agents are added in the presence of sodium sulfite to prevent the formation of colored oxidation products of the latter agents. Sulfite does not protect Phenidone from yellow-orange discoloration, although it does prevent the green color from forming, and the sulfite does not influence the kinetics of development by Phenidone except by way of silver halide solvent action.

Some experiments were carried out to determine whether the developer activity of the ascorbic acid was sufficient to account for the superadditivity once the charge effect was neutralized. The rate of development at pH 7.25 in the presence of the quaternary salt, dodecyl pyridinium *p*-toluenesulfonate, is not sufficient. However, previous work had shown⁹ that the emulsion speed which can be obtained with an ascorbic acid developer used under optimum conditions is only about one-half that obtained with a hydroquinone or Metol developer, or with a Phenidone developer, and presumably the ascorbic acid will not develop as small latent-image specks as the other developers. Accordingly, a predevelopment test was carried out as follows: Exposed film was developed in a Phenidone solution at pH 7.6 to give a density of 0.58. The film was then washed repeatedly in water, soaked one-half hour in a solution of 0.001 M dodecyl pyridinium *p*-toluenesulfonate, and then transferred to a 0.005 M solution of *d*-araboascorbic acid containing 0.001 M dodecyl pyridinium salt at pH 7.25. Figure 7 shows the curve obtained (Curve 3). Curve 1 of this figure represents development by Phenidone alone at this pH. Curve 2 represents development by the mixture. Curve 4 was obtained by subtracting Curve 1 from Curve 2, and is thus the superadditive density curve in terms of time of development. If Curve 3 is shifted along the time axis to the point where the density of 0.58 coincides with Curve 4, it is found that the entire curve coincides with Curve 4 over the density range the two have in common. It is thus apparent that, once development has been started in the active Phenidone developer, the ascorbic acid can continue development at a high enough rate to account

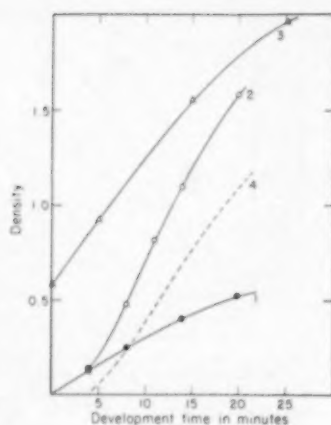


Fig. 7. Development by Phenidone + *d*-araboascorbic acid. Curve 1, Phenidone alone; 2, mixture; 3, predevelopment in Phenidone followed by development in *d*-araboascorbic acid + dodecyl pyridinium salt solution; 4, Curve 2 minus Curve 1.

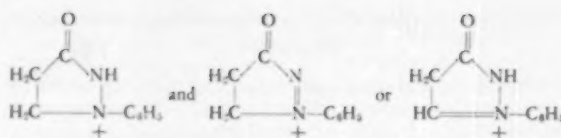
for the superadditive properties of the mixture, providing Phenidone in some way reduces the charge effect to the same extent that the quaternary salt does.

Diaminodurene-Hydroquinone Monosulfonate and Metol-Hydroquinone Monosulfonate Mixtures

A few experiments were carried out with mixtures of diaminodurene and hydroquinone monosulfonate and of Metol and hydroquinone monosulfonate at pH 9.4. The results obtained with the first mixture are illustrated in Figure 8. Definite superadditivity was obtained, but the activity of the hydroquinone monosulfonate alone is more than sufficient to account for the superadditivity when the charge effect is sufficiently reduced. Similar results were obtained with the Metol-hydroquinone monosulfonate mixture, except that the superadditivity was not as great.

Discussion

Apparently agents such as ascorbic acid and hydroquinone can act to regenerate Metol and Phenidone in a partially oxidized solution, but such regeneration causes superadditive properties only under certain conditions and is not a general cause. The superadditive effects obtained with the Phenidone-ascorbic acid and Phenidone-hydroquinone monosulfonate mixtures can be explained on the following basis: (1) Phenidone, which is uncharged at low pH and at most singly ionized at high pH, can readily initiate development of the latent-image specks. As the specks increase in size, the charge barrier^{5,6} in the vicinity decreases, permitting an increase in the concentration of the doubly or triply charged developer ions at the surface and an increase in the concentration of such ions adsorbed by the silver bromide. (2) In its reaction with the silver bromide, Phenidone forms an intermediate oxidation product which is a quaternary ion bearing a positive charge. Such an ion, adsorbed by the silver bromide, further decreases the charge barrier and promotes adsorption of the negatively charged developing agents. Possible structures of this ion are (corresponding to two different oxidation stages):



Metol may form a positively charged oxidation product of the structure:



The weaker superadditivity of the Metol-hydroquinone monosulfonate combination can be attributed to the smaller importance of (2) because of lower stability of the quaternary ion or reduced formation of the ion because of action of the sulfite. It has been shown that in all of the combinations studied, the formation of a quaternary ion of activity equal to dodecyl pyridinium ion would suffice or more than suffice to account for the superadditivity of the combination.

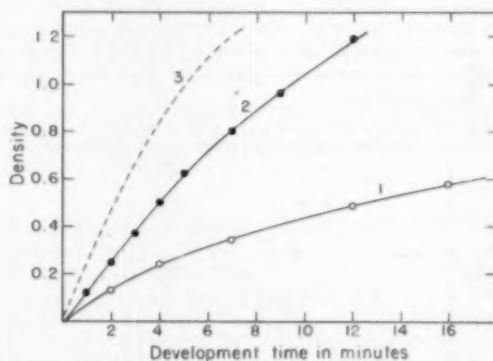


Fig. 8. Development by diaminodurene + hydroquinone monosulfonate, pH 9.4; Log *E* 1.75. Curve 1, 0.00025 *M* diaminodurene; 2, 0.00025 *M* diaminodurene + 0.005 *M* hydroquinone monosulfonate; 3, 0.005 *M* hydroquinone monosulfonate + 0.001 *M* dodecyl pyridinium salt.

References

1. G. I. P. Levenson, *Phot. J.*, Vol. 89B, p. 13 (1949).
2. J. E. LuValle, *J. Am. Chem. Soc.*, Vol. 74, p. 2970 (1952).
3. T. H. James, *J. Phys. Chem.*, Vol. 43, p. 701 (1939).
4. T. H. James, *PSA Journal (Phot. Sci. and Tech.)*, Vol. 16B, p. 83 (1950).
5. T. H. James, *J. Franklin Inst.*, Vol. 240, p. 15 (1945); *J. Phys. Chem.*, Vol. 55, p. 563 (1951).
6. A. Weissberger, S. D. Thomas, and J. E. LuValle, *J. Am. Chem. Soc.*, Vol. 65, p. 1489 (1943).
7. J. D. Kendall, *Brit. Patent* 542,502 (1942); U. S. Patent 2,289,367 (1943).
8. J. D. Kendall, *Brit. J. Phot.*, Vol. 100, p. 56 (1953).
9. T. H. James, *J. Franklin Inst.*, Vol. 239, p. 41 (1945).

PHOTOGRAPHY IN COMBUSTION STUDIES

Harry Williams and A. Greenville Whittaker*

IN 1950 THIS GROUP became interested in the study of combustion of liquid mixtures. Results of some of the work have already been published¹. Using a window bomb similar to B. L. Crawford's² at the University of Minnesota, photographs were made of the burning of liquids in small glass tubes and the rates of combustion were determined with satisfactory precision. An earlier publication³ indicated that good photographs could be obtained by backlighting the samples and using a revolving drum camera. It was felt at NOTS that pictures of equal quality could be obtained by a similar method and such was the case.

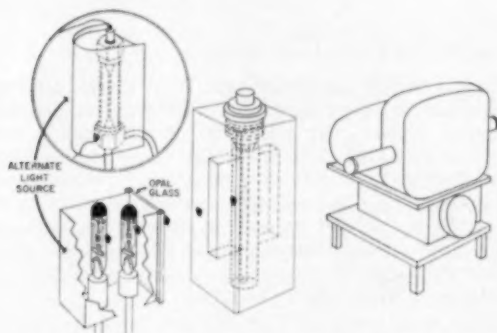


Fig. 1. Diagram of camera and lighting arrangement for high-speed photography of liquids burning in test tubes. Released if credit given as follows: "Official Photograph U. S. Navy."

Apparatus

The apparatus consisted of a two-window bomb, the windows of which were constructed from Lucite or plexiglass, a pressurizing system, a high speed 16mm motion picture camera and two types of light sources. Samples were burned in a 4mm I.D. heat resistant glass test tube at pressures ranging from 150 psig to a maximum of 4500 psig. The light sources used were (a) two 1000-watt projection lamps mounted in line with the sample and camera so that the light passes through the sample to the camera or (b) a 2000-watt high pressure mercury arc mounted similarly. An opal glass diffusion screen was mounted between the lamp and bomb to minimize hot spots on the film. The light sources were approximately five inches from the object and the camera was mounted with about fifteen inches object to film distance. Figure 1 shows a sketch of the layout of the apparatus with light sources and camera. The camera has a $f/2.7$ anastigmat lens of 63mm focal length

and nearly all pictures are taken with maximum aperture. Using a Weston light meter the following readings were obtained as the maximum light values at a point eight inches in front of the lens.

Lamp	Meter reading
2000-watt mercury arc	1600
Two 1000-watt incandescent lamps	800

These values permitted a framing speed of about 1000 to 2500 for the mercury arc, and 300 to 900 for the incandescent lamps.

Timing was accomplished either by using the normal built-in timing light and a pulse generator or in the case of high speed color film as follows: a 300-watt projection lamp using a slotted disc as a chopper produced light pulses which were introduced into the camera by means of a series of lenses and a small tapered Lucite rod so that the light pulses impinged on the edge of the film.

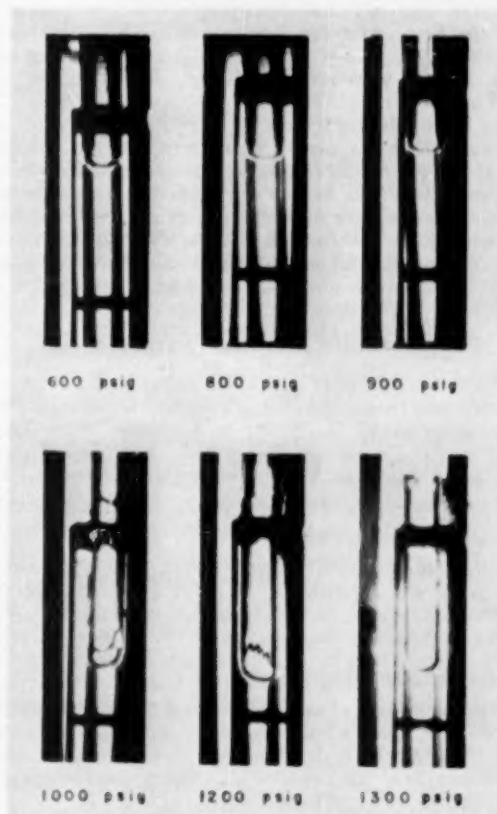


Fig. 2. Photographs obtained using the arrangement shown in Figure 1. "Official Photograph U. S. Navy."

* U. S. Naval Ordnance Test Station, Inyokern, Post Office, China Lake, California. Presented at the PSA National Convention in Los Angeles, California 8 August 1953. Received 28 August 1953.

Results

Using this apparatus pictures were obtained of very good quality which gave a good deal of information on the processes occurring during the combustion of liquids in small tubes. Figure 2 shows some of the pictures obtained. Black-and-white film was used in the early part of the work but color film gave a better record of what was going on during the combustion process. More recently only color film has been used in this work. At first the pictures were made at framing speeds of 200 to 300 but these films did not slow down the action

sufficiently. At present framing speeds from about 500 to 2500 frames per second are used. Attempts are being made to improve the resolution of the pictures obtained.

References

1. "Some Measurements of the Burning Rates of Mixed Liquid Bipropellants," C. W. Tait, A. G. Whittaker, Harry Williams, J. Am. Roc. Soc., Vol. 85, p. 83 (1951).
2. Crawford, B. L., Jr., et. al., "Direct Determination of Burning Rate of Propellant Powders," Anal. Chem., Vol. 19 (1947), pp. 630-33.
3. Stocks, G. W., and L. A. Wiseman, "The Combustion of Liquid Monopropellants." Part I, ERDE Report No. 31/R/49.

NEW STANDARDS FOR PHOTOGRAPHY

Carolyn Locher*

NATIONAL STANDARDS in the field of photography are approved through the voluntary procedures of the American Standards Association, Incorporated. A number of new photographic standards and revisions of existing American Standards for photography are now available from the Association headquarters at 70 East 45th Street, New York 17, New York. Recent approvals bring the total to 150 standards, exclusive of motion picture standards.

The Photographic Society of America participated in the work of four national committees which developed and approved the photographic standards. Along with representatives from industry, from distributor organizations, consumers, those with a general interest, the PSA representatives contributed to the work of standards development and helped in the establishment of a national consensus on the topics concerned.

Physical and Chemical Characteristics

ASA Sectional Committee PH1 on Physical and Chemical Characteristics of Films, Plates and Papers has PSA representatives R. G. Bowie of Rochester, New York and David B. Eisendrath, Jr., of Brooklyn, New York as members. American Standards recently completed by that committee include:

AERIAL FILM SPOOL DIMENSIONS

Eight standards (PH1.2-1952 to PH1.9-1952, inclusive) governing the dimensions of eight sizes of daylight loading film spools for use in aerial cameras. Price 25 cents each.

AERIAL FILM AND TRAILERS

The dimensions of aerial films and their unsensitized leaders and trailers are covered by American Standard PH1.10-1952 which deals with the four widths most commonly used for civilian and military photography from the air. Price 25 cents.

* American Standards Association, Incorporated, 70 East 45th Street, New York 17, New York. Received 15 September 1953.

PHOTOGRAPHIC PAPER DIMENSIONS

Three existing standards have been revised and approved as two new American Standards for standard sizes and dimensional tolerances of sensitized papers. American Standard Dimensions for Photographic Paper Rolls PH1.11-1953 (Revision of Z38.1.5-1943 and partial revision of Z38.1.6-1943) is timely in view of the increasing use of roll papers for automatic processing. American Standard Dimensions for Photographic Paper Sheets PH1.12-1953 brings up to date two previous standards. Price of each 25 cents.

Photographic Sensitometry Standards

PSA representative H. R. Sprentall of Rochester, New York is Chairman of ASA Sectional Committee PH2 on Photographic Sensitometry. Another PSA representative on this Standards Committee is Allen G. Stimson of West Lynn, Massachusetts. Some of the most important American Standards, from the standpoint of fundamental applications to photography, and some of the standards most difficult to achieve, are within the province of Sectional Committee PH2. Their recently approved standards are:

FOR DENSITOMETRY OF COLOR FILMS

American Standard Spectral Diffuse Densities of Three-Component Subtractive Color Films, PH2.1-1952, an important milestone in the progress of color photography. Price 35 cents.

PHOTOGRAPHIC PAPER GRADING

This is an extension and revision of Z38.2.3-1947 to include a new method of photographic paper sensitometry proposed by the National Bureau of Standards. It incorporates a method for distinguishing the grades of papers that should be useful in purchase specifications. Twelve pages, price 50 cents.

PHOTOGRAPHIC SCIENCE AND TECHNIQUE

Photographic Apparatus Standards

Sectional Committee PH3 on Photographic Apparatus is headed by Frank E. Carlson, Hon. PSA, APSA of East Cleveland, Ohio, the PSA representative. Standards of immediate interest and importance to photographers when they go to purchase cameras and accessories, printers, projectors and other viewing equipment are the concern of this committee. Recently completed standards are:

TRIPOD CONNECTIONS, SMALL SCREW

A revision of the old American Standard Tripod Connections for American Cameras, $\frac{1}{4}$ inch-20 Thread (Z38.4.1-1942) has been completed. Published under the new series number PH3.6-1952, this standard incorporates changes making for greater clarity and precision without altering the limits set forth in the original American Standard. Price 25 cents.

TRIPOD CONNECTIONS, LARGE SCREW

An amplification and revision of the earlier standard Z38.4.2-1942, this standard is titled "Tripod Connections for Heavy-Duty or European Cameras, $\frac{3}{8}$ inch-16 thread with adapter for $\frac{1}{4}$ inch-20 Tripod Screws." Price 25 cents. The number is PH3.7-1952.

ROLL FILM CAMERA WINDOWS

This revision of Z38.4.9-1944 governs the size and location of the windows (usually red) in camera backs to insure that the exposure numbers printed on the backing paper will be visible and the resulting exposures will be correctly spaced on the film. The revised standard is PH3.1-1952 American Standard Back Window Location for Roll Film Cameras and the price is 25 cents.

THREADS FOR LENS ATTACHMENTS

American Standard Specifications for Attachment Threads for Lens Accessories PH3.12-1953 is a revision of a previous standard setting limiting dimensions that assure correct fitting of lens accessories, such as filters, sun shades and supplementary lenses that screw into the front lens barrel. Price 25 cents.

STEREO STILL PICTURE STANDARDS

One of the signal accomplishments of the national standards program in the field of photography is this agreement by all interested parties on one standard format for stereo pictures made on 35mm film in the place of the several, noninterchangeable forms that had begun to appear in American stores. Ask for American Standard Stereo Still Pictures on 35mm Film (5-Perforation Format), PH3.11-1953. Price 25 cents.

MASK DIMENSIONS FOR CONTACT PRINTS

Picture sizes, when they are determined by masks used in contact printing from roll film negatives, are governed by American Standard PH3.9-1953. This revision of an earlier standard (Z38.7.12-1944) is titled "Specifications for Masks (Separate) for Use in Photographic Contact Printing." Price 25 cents.

CONTACT PRINTER STANDARDS

The quality and performance of contact printers for amateur and professional use (exclusive of graphic arts and special purpose printers) are covered by PH3.8-1953 American Standard Specifications for Contact Printers. Price 25 cents.

Photographic Processing Standards

Another ASA Sectional Committee in the field of photography on which the official PSA representative serves as Chairman is ASA PH4 on Photographic Processing with John I. Crabtree, FPSA, of Rochester, New York as Chairman. Standards for photographic processing supplies, equipment, and procedures are the concern of this committee which has charge of a large number of American Standards that directly concern photographic workers. Recently approved American Standards developed by Mr. Crabtree's committee include:

TANKS FOR SHEET FILM

This revision of Z38.8.15-1949 defines the inside dimensions of tanks for processing sheet films or plates up to 8 x 10 inches in size when the sensitized materials are held in hangers covered by American Standard Specifications for Channel-Type Photographic Hangers, PH4.4-1952. Ask for American Standard Specifications for Sheet Film Processing Tanks, PH4.2-1952. Price 25 cents.

PHOTOGRAPHIC TRAYS

Many years of patient work went into this new American Standard PH4.3-1952 titled "Specifications for Photographic Trays." Trays manufactured in compliance with this Standard will have the correct dimensions, design, construction and quality for safe and efficient darkroom use. The principal American manufacturers of photographic trays participated in the work of developing the Standard and approved it prior to issue. Price 25 cents.

FILM DEVELOPING HANGERS

American Standard Specifications for Channel-Type Photographic Hangers for Plates and Sheet Film, PH4.4-1952 is a new standard specifying the dimensions and characteristics of satisfactory hangers for processing eleven sizes of sheet film or plates. Price 25 cents.

PHOTOGRAPHIC GRADE BLOTTERS

For the first time the requirements, both chemical and physical, for blotting papers used for drying photographic prints have been recognized on a national basis. American Standard Photographic Grade Blotters PH4.10-1953 represents a national consensus of producers, consumers, distributors, and other interests. Price 25 cents.

SODIUM ACID SULFATE

The requirements to be met by sodium acid sulfate, fused (NaHSO_4), to qualify as "Photographic Grade" material suitable for use in photographic processing

baths are established in ASA PH4.105-1952. Standard specifications of this type are seldom of direct interest to practicing photographers but they are of considerable indirect benefit. In the hands of chemical manufacturers and firms who package chemical formulations for photographic use, standards such as this are of particular merit because they spell out the special requirements of chemicals used for photographic processing. Often "chemically pure," "reagent grade," U.S.P., and other labels denoting purity and strength of chemicals are not strict enough to provide materials suitable for photographic use. Price 25 cents.

SODIUM SULFITE

Another American Standard for a "Photographic Grade" chemical, issued as PH4.275-1952, is a revision of the earlier standard Z38.8-275-1948. Purity standards are established and test methods prescribed for certain inert or photographically harmful impurities. Price 25 cents.

AMMONIUM CHLORIDE

Requirements for this ingredient of rapid fixing bath compounds are covered by PH4.183-1953 "American Standard Specification for Photographic Grade Ammonium Chloride NH_4Cl ." Price 25 cents.

AMMONIUM SULFATE

American Standard Specification for Photographic Grade Ammonium Sulfate $(\text{NH}_4)_2\text{SO}_4$ limits the photographic impurities for this familiar tropical processing agent. Ask for ASA PH4.184-1953. Price 25 cents.

Professional Motion Picture Standards

The Photographic Standards Board of the American Standards Association, which serves as a general administrative committee for photographic standards activities, recently approved a new Scope for Sectional Committee PH22 on Motion Pictures. The new Scope was proposed to recognize the dependence of the television industry on professional motion picture production and exhibition methods, materials and apparatus. The newly revised Scope is as follows:

Define technical terms and prepare engineering standards for the field of motion pictures and for those segments of television and theatre television that use techniques adapted from the motion picture industry.

The Photographic Society of America was represented on Motion Picture Standards Sectional Committee PH22 by invitation. The late Kenneth Shaftan of Long Island City, New York actively participated in the affairs of the Committee which recently completed the following American Standards:

ANOTHER 35MM PERFORATED FILM

Groping the way back to a single standard for perforated 35mm motion picture film (which was official from 1941 to May 15, 1944 for the "positive type" perforation but abandoned because one California company continued to use the old Bell & Howell method of perforating), a third American Standard perforation for 35mm film was approved by PH.22 as PH22.1-1953 and was

Subtitled "Alternative Standards for Either Positive or Negative Raw Stock". The new perforating dimensions are already being followed in the case of color films. The dimensional differences between the third American Standard 35mm film and the two previous American Standards for positive film and negative film respectively, are unimportant in still photography. Price of the standard, 25 cents.

SPLICES FOR 16MM FILM

A new standard, PH22.24-1952, Splices for 16 millimeter Motion Picture Films for Projection, supersedes Z22.24-1941, Z22.25-1941, and the War Standard Z52.20-1944. Price 25 cents.

SPLICES FOR 8MM FILM

Dimensions for splices for this strictly amateur film for the first time are recognized in an American Standard. "Splices for 8mm Motion Picture Films" PH22.77-1952 which sells for 25 cents a copy.

PROJECTOR LAMP DIMENSIONS

American Standard Dimensions for Projection Lamps, Medium Prefocus Ring Double-Contact Base-Up Type for 16mm and 8mm Motion Picture Projectors, PH22.84-1953 establishes the dimensions essential for interchangeability. Price 25 cents.

American Standard PH22.85-1953 covers the same ground for lamps having a single contact on the bottom of the base. Price 25 cents.

PUBLISHED FOR TRIAL AND CRITICISM

THE PROPOSED AMERICAN STANDARD Specification for Photographic Filter Sizes, PH3.17, has been under consideration for the past two years by the Subcommittee on Optics and Lenses, PH3-3, of the ASA Sectional Committee on Photographic Apparatus, PH3.

Initially, various producers were canvassed to determine the filter sizes most commonly available. It was clear from the mass of data collected that there were many filters differing only slightly in their external dimensions. Accordingly, a list of filter sizes was prepared which it is believed constitutes the minimum number capable of meeting the various requirements at the present time.

The preferred standard dimensions (2.1) may apply to both mounted and unmounted filter disks. It is hoped that ultimately it may be possible to drop the secondary standard dimensions (2.2) and rely solely on the preferred standard dimensions. This may not be possible for several years, but it is believed that publication of the standard may in time lead to this simplification.

THE PROPOSED AMERICAN STANDARD for the internal synchronization of front shutters was developed by Subcommittee PH3-1 on Cameras and Related Apparatus. All interested manufacturers of cameras, shutters, and flash lamps in the USA participated in this work. Nevertheless the committee has decided to seek reactions to the proposal from the widest possible audience before recommending approval as an American Standard.

Comments and suggestions relating to both proposed standards should be sent to the American Standards Association, Incorporated, 70 East Forty-fifth Street, New York 17, N.Y. before 1 February 1954.

J. W. Mc NAIR

Proposed American Standard

Specification for Photographic Filter Sizes

ASA
Reg. U. S. Pat. Off.
PH3.17
First Draft
November 1953

Page 1 of 2 pages

1. Scope

1.1 This proposed standard applies only to the physical dimensions of photographic filters, either mounted or unmounted. It is applicable to all types of filters, including solid glass, plastic between glass, and gelatin wafer filters.

2. Filter Dimensions

2.1 Preferred Standard

2.1.1 Filter Disk

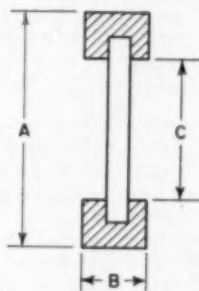


Fig. 1

Filter Size Designator (Series)	Diameter A	Thickness B	Full Aperture C (Minimum Value)
IV ($1/16$)	0.812	0.160	0.688
V ($1^3/16$)	1.188	0.170	1.062
VI ($1^5/8$)	1.625	0.190	1.500
VII (2)	2.000	0.210	1.875
VIII ($2^1/2$)	2.500	0.220	2.375
IX ($3^1/4$)	3.250	0.220	3.125

Tolerances on diameter, A: ± 0.008 inch
Tolerances on thickness, B: ± 0.010 inch

All dimensions given in inches.
These filter dimensions are not restricted to mounted filters; moreover, these are preferred standard dimensions. They may be used for either solid or laminated filters.

2.2 Secondary Standards

2.2.1 Unmounted Solid Glass Round Filter

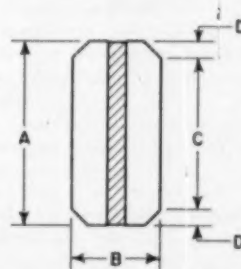


Fig. 2

Filter Size Designator (Milli-meter)	Diameter A (Inch)	Thickness B (Inch)	Break, or Ground Edge D (Inch)
19	0.748	0.050	This shall be such that $2D \leq 0.020$ inch where $2D = A - C$
21.5	0.846	0.050	
25	0.984	0.050	
26.5	1.043	0.050	
31.5	1.240	0.050	
33	1.299	0.050	
39	1.535	0.050	

Tolerances on diameter, A: ± 0.008 inch
Tolerances on thickness, B: ± 0.020 inch

Published for Trial and Criticism by the American Standards Association, Incorporated
70 East Forty-fifth Street, New York 17, N. Y.
Sponsor: Photographic Standards Board

NOT APPROVED

Price 25 cents

2.2.2 Unmounted Laminated Round Filler

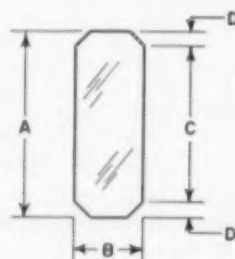


Fig. 3

2.2.3 Unmounted Square Filler

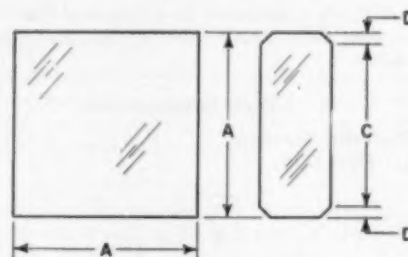


Fig. 4

Filter Size Designator	Diameter A	Thickness B	Break, or Ground Edge D
3/4	0.750	0.120	This shall be such that $2D \leq 0.020$ inch where $2D = A - C$
1	1.000	0.130	
1 1/4	1.250	0.130	
1 1/2	1.500	0.130	
1 3/4	1.750	0.130	
2	2.000	0.155	
3	3.000	0.190	
4	4.000	0.190	
5	5.000	0.190	

Tolerances on diameter, A: ± 0.008 inch
Tolerances on thickness, B: ± 0.010 inch

All dimensions given in inches.

Filter Size Designator	Width A	Thickness B	Break, or Ground Edge D
2	1.992	0.183	This shall be such that $2D \leq 0.020$ inch where $2D = A - C$
3	2.992	0.183	
4	3.992	0.183	
5	4.992	0.183	

Tolerances on width, A: ± 0.008 inch
Tolerances on thickness, B: ± 0.010 inch

All dimensions given in inches.

PH3.17

NOT APPROVED

for the Internal Synchronization of Front Shutters

1. Scope and Purpose

1.1 The purpose of this standard is to establish criteria for classifying and testing the operation of front shutters with built-in electrical contacts for synchronizing flash lamps.

1.2 This standard describes the classification of front shutters according to the type of synchronization available.

1.3 The various factors in a shutter which control synchronization are given limiting functional values.

1.4 Test methods for determining the synchronizing performance of a shutter are set up.

2. Definitions

2.1 Classification. Classification is the designation of the synchronization class to which a shutter belongs according to the type of flash lamp or lamps which may be properly synchronized at all of the marked speeds of 1/200 second or slower.

2.2 Delay Time. Delay time is the time from the initial closing of the shutter contacts to the first fully open position of the shutter blades at the maximum diameter of the free opening of the shutter without optics.

2.3 Shutter-Contact Duration. Shutter-contact duration is the time from the initial closing of the shutter contacts to their final opening.

2.4 Efficiency of the Shutter Contacts. Efficiency of the shutter contacts is the ratio of the energy the contacts actually pass to the energy they would pass if there were no rebound or change in resistance in the system during the first $2\frac{1}{2}$ milliseconds of the contact cycle.

2.5 Contact Insulation Value. Contact insulation value is the resistance between open contacts or between the shutter case and all contacts which are insulated from it. This resistance shall remain unchanged except during the tripping cycle.

3. Classification of Synchronized Shutters

3.1 X-type Synchronized Shutters. X-type synchronized shutters are designed primarily for the operation of electric discharge tubes of the direct triggering type.

Delay Time: 0 ± 1 millisecond. (In all cases the shutter must be at least 80 percent open at the time of first contact closure.)

Contact Duration: 1 millisecond (min)

Contact Efficiency: 30 percent (min)

Contact Insulation Value: 3 megohms at 85 percent relative humidity

3.2 XS-type Synchronized Shutters. XS-type synchronized shutters are designed for the operation of electric discharge tubes and flash lamps at selected shutter speeds.

Delay Time: 0 ± 1 millisecond. (In all cases the shutter must be at least 80 percent open at the time of first contact closure.)

Contact Duration: $2\frac{1}{2}$ milliseconds (min)

Contact Efficiency: 70 percent (min)

Contact Insulation Value: 3 megohms at 85 percent relative humidity

3.3 F-type Synchronized Shutters. F-type synchronized shutters are designed primarily for the operation of F-type flash lamps.

Delay Time: $3 \pm 2 - 1$ millisecond

Contact Duration: $2\frac{1}{2}$ milliseconds (min)

Contact Efficiency: 70 percent (min)

Contact Insulation Value: 3 megohms at 85 percent relative humidity

3.4 M-type Synchronized Shutters. M-type synchronized shutters are designed primarily for the operation of M-type flash lamps.

Delay Time: 15 ± 2 milliseconds

Contact Duration: $2\frac{1}{2}$ milliseconds (min)

Contact Efficiency: 70 percent (min)

Contact Insulation Value: 3 megohms at 85 percent relative humidity

3.5 XF-, XM-, FM-type Two-Point Synchronized Shutters. XF-, XM-, FM-type two-point synchronized shutters are combinations of 3.1 and 3.3, 3.1 and 3.4, and 3.3 and 3.4 in one shutter.

3.6 Three-Point Synchronized Shutter. The three-point synchronized shutter is a combination of X, F, and M (as shown in 3.1, 3.3 and 3.4) in one shutter.

3.7 Fully Synchronized Shutter. The fully synchronized shutter is a combination of X, F, and M (as shown in 3.1, 3.3 and 3.4) in one shutter, providing for zero delay and for an adjustable delay with a minimum range from 5 to 13 milliseconds in order to properly

synchronize all types of electric discharge tubes and flash lamps throughout the marked shutter speed range.

Page 2 of 3 pages

4. Equipment

4.1 In general, the same equipment that is specified in 3.1 of American Standard Method for Determining Performance Characteristics of Between-the-Lens Shutters Used in Still Picture Cameras, PH3.4-1952, can be used with certain minor modifications or additions. All precautions listed in the Appendix of PH3.4-1952 should be observed.

5. Test Methods

5.1 **X-type Contacts.** The test equipment described in 3.1 of American Standard Method for Determining Performance Characteristics of Between-the-Lens Shutters Used in Still Picture Cameras, PH3.4-1952, is used, except that the photocell load resistor is tapped 10 to 20 percent above the ground and the shutter contacts are connected between this tap and the ground.

When the shutter contacts close, the characteristic shutter trace is depressed between h and i as shown in Fig. 1.

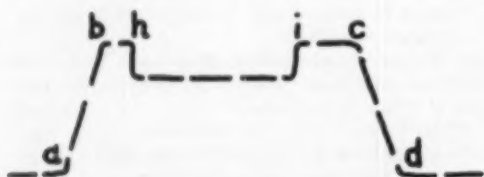


Fig. 1

Here the contacts closed after the first fully open position. If the contacts had closed before the first fully open position, the trace would be as shown in Fig. 2.

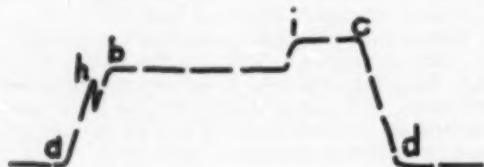


Fig. 2

In both cases the location of h with respect to b is important, and the time between points b and h is the significant value.

5.2 **F- and M-type Contacts.** The test equipment described in 3.1 of American Standard Method for Determining Performance Characteristics of Between-the-Lens Shutters Used in Still Picture Cameras, PH3.4-1952, is used and the shutter contacts are connected between ground and the external trigger post, as described in section (b) of the Appendix to PH3.4-1952. A typical trace is shown in Fig. 3.

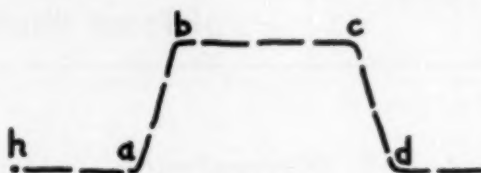


Fig. 3

Here the time between points h and b is the significant value.

5.3 **Contact Duration.** Here the photocell input circuit is replaced by a d-c source as shown in Fig. 4.

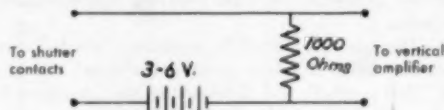


Fig. 4

The resulting trace is of the type shown in Fig. 5.

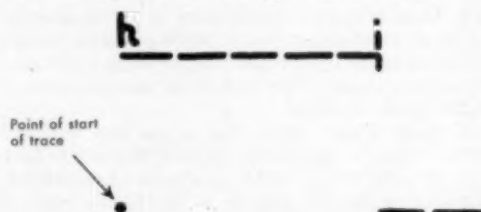


Fig. 5

If the shutter is of the type where the contacts remain closed while the blades are open, or until the tripping lever is released, the trace is a straight line at the level of h.

The time between h and i is the significant value.

Note: Because of bounce or other source of poor contact, the trace between h and i may show discontinuities, other than the timing pulse, and considerable microphonic "grass." Once the contact duration has been established, the modulation may be turned off and the quality of the contact may be seen more clearly.

5.4 Contact Efficiency

5.4.1 Here the photocell input circuit is replaced by a controlled capacitor changing circuit, as shown in Fig. 6.

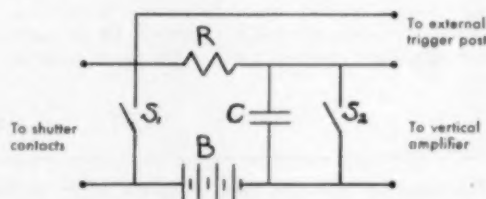


Fig. 6

B: 6 v "hot-shot" type battery

R: 2-ohm, 20-watt non-inductive resistor (2 ft of 1-ohm Nichrome or similar wire) of sufficient size to minimize changes in resistance caused by heating when cycled rapidly

S₁: Normally open mercury switch or equivalent

S₂: 100-watt snap switch

C: 4000-microfarad, 10 to 15 v electrolytic capacitor

A suitable reticle for the oscilloscope tube will aid greatly in this test. The following form, as shown in Fig. 7, is suggested.

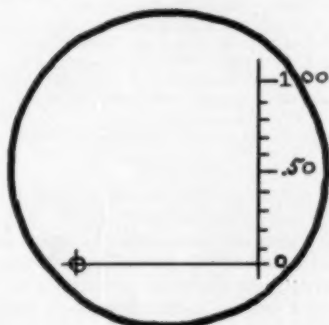


Fig. 7

5.4.2 Cycle of Operation

(a) Adjust the sweep frequency and X-gain of the oscilloscope so that the reticle reference lines are $2\frac{1}{2}$ milliseconds apart; then turn off the Z modulation.

(b) Close S₂ to discharge C completely; then open S₂.

(c) Close S₁ and note where the trace crosses the percent line; then adjust the Y-gain of the oscilloscope to make the trace cross the percent line at 100 percent.

(d) Repeat operations (b) and (c) until the conditions described are achieved. The test unit is now ready for use.

(e) Connect the shutter and repeat operation (b).

(f) Trip the shutter and note where the trace crosses the percent line. This is the "contact efficiency" in percent.

5.4.3 Precautions

(a) It is advisable to put the rated potential on the capacitor, C, for some time (15 minutes minimum) before starting a series of tests in order to reform the electrolytic plates.

(b) S₁ should be a mercury switch in which the mercury actually wets the leads.

(c) Care must be exercised to bring the start of the trace to the zero-zero point.

(d) In 5.4.2, operation (b), it may be necessary to leave the switch closed for as much as 30 seconds to discharge C completely, particularly when the contact duration has been long.

5.4.4 Other Measurements. As a matter of general information, it should be noted that measurements of static contact resistance are no criterion for actual contact performance.

6. Contact Insulation Value

6.1 The resistance between open contacts or between the shutter case and all contacts insulated from it is measured at 500 volts by a suitable commercial instrument, such as a "Megger" (James G. Biddle, Catalogue No. 8676), or equivalent, to an accuracy of ± 20 percent.

6.2 Eighty-five percent relative humidity may be obtained by placing the shutter over a saturated solution of potassium bromide in a closed container. Conditioning time is 48 hours.

6.3 To maintain the proper relative humidity conditions, an excess of chemical crystals must be present at all times.

6.4 Shutters should be tested while at 85 percent relative humidity.

DEVELOPERS FOR USE IN DETERMINING THE DISTRIBUTION OF THE LATENT PHOTOGRAPHIC IMAGE

T. H. James, W. Vanselow, and R. F. Quirk*

ABSTRACT

Metol and *d*-araboascorbic acid form a developer combination at pH 9-10 which is reasonably stable in air in the absence of sulfite and does not form colored oxidation products. The following formula is suggested for a high-speed developer for surface latent image: Metol, 2.5 grams; *d*-araboascorbic acid, 10.0 grams; potassium bromide, 1.0 gram; α -picolinium- β -phenylethyl bromide, 0.5 gram; Kodalk, 35 grams; 0.1 percent phenosafranin solution, 5 cc.; and water to make 1 liter. The phenosafranin serves to suppress aerial fog, and can be omitted when slow positive materials are developed. The developer can be converted to an internal latent-image developer of comparable activity by the addition of hypo.

THE PROBLEM of how to determine the distribution of latent image between the surface and the interior of the photographic grains is an important one in photographic theory, but a quantitative method is still lacking. We may define surface latent image as that latent image which makes direct physical contact with any solution surrounding the silver halide grain when there is no solvent action at the silver halide surface. Similarly, we may define internal latent image as that latent image which will not make contact with such a solution because it is covered with silver halide. Practically, we must include in the definition, at the present time, a statement of the developers used to detect the two kinds of latent image, and the bleach used to destroy the surface latent image.

Several developers and methods of detection have been used. Kornfeld¹ used postfixation physical development to determine total image (surface plus internal) and the same development after a bleaching treatment to determine internal latent image alone. The surface latent image was destroyed by bleaching it in potassium persulfate solution before fixation and physical development in the determination of the internal image. Berg and Ford² used prefixation physical development in a solution which contained no silver halide solvent to determine surface latent image, and postfixation physical development in the same solution to determine total image. Internal image was determined by bleaching the surface image in acid bichromate solution, followed by fixation and physical development.

In most of the work reported in the literature, chemical development has been used. Hautot and his co-workers³ used a ferro-oxalate developer to determine surface image, chromic acid bleaches to destroy surface image, and *p*-phenylenediamine developers to determine internal image. Stevens⁴ and his co-workers used a *p*-hydroxyphenylglycine developer containing no sulfite to determine surface image, an acid bichromate bleach to destroy surface latent image, and a Metol-hydroquinone developer containing sodium thiosulfate to determine internal latent image.

There are disadvantages to all of the methods mentioned. Physical development yields lower emulsion speeds than chemical development, and hence probably does not utilize all of the latent-image nuclei which are active in promoting chemical development. Moreover, physical development is more difficult experimentally, particularly with emulsions of relatively high iodide content. The surface developers which have been used for chemical development (ferro-oxalate and *p*-hydroxyphenylglycine) are not the same as those used for internal development (*p*-phenylenediamine and the Metol-hydroquinone combination) and show definite differences in activity. The physical development methods tend to determine the number of latent-image centers, whereas the chemical development methods tend to determine the number of developable grains. Under most practical conditions, however, the developed density is only roughly proportional to the number of developed silver particles, and the proportionality factor will be the same for surface and internal image only if the effective size of the developed particles is the same for both.

It is desirable in latent-image distribution work to use developers of essentially the same activity for surface and internal latent-image development. A combination of Metol developing agent and *d*-araboascorbic acid (isoascorbic acid) has proved quite satisfactory for this purpose in our tests, both with positive- and with negative-type emulsions. This developer can be used in the complete absence of sulfite and is without significant solvent action on silver halide. Addition of sodium thiosulfate converts it to an internal developer. The *d*-araboascorbic acid acts essentially as a preservative to prevent the accumulation of oxidation products of the Metol.

Experimental Procedure and Results

Two standard motion-picture positive films and one high-speed negative film were used to test the developers. Exposures were made under standard conditions on the Eastman IIb Sensitometer. Development was carried out in a 4-liter tank at 20 C., using mechanical agitation. No attempt was made to remove the air already in the water or to exclude air from contact with the solutions

* Research Laboratories, Eastman Kodak Company, Rochester 4, New York. Communication No. 1593 from the Kodak Research Laboratories. Received 20 July 1953.

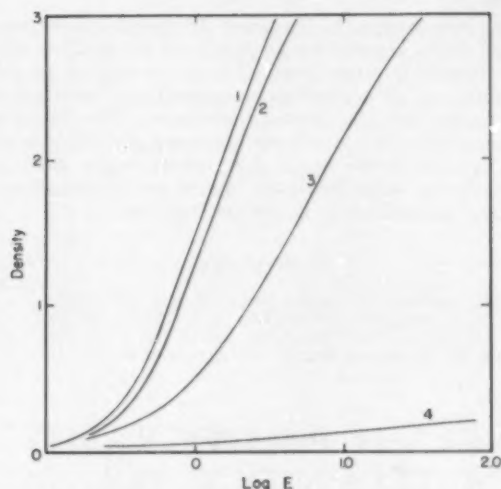


Figure 1. Characteristic curves for the development of motion-picture positive film in: (1) D-19 6 minutes, fog 0.06; (2) M-AA-2 24 minutes, fog 0.05; (3) glycine 6 minutes, fog 0.06. Curve 4 represents internal image development by D-19 in 6 minutes.

at any time. The solutions, however, were made up within an hour or two before use.

Several developer formulas with Metol developing agent and *d*-arabascorbic acid were tested. In general, the best results were obtained with a solution of the following basic formula:

M-AA-1	
Metol	2.5 grams
<i>d</i> -Arabascorbic acid	10.0 grams
Potassium bromide	1.0 gram
Kodalk-balanced alkali	35.0 grams
Water to make	1.0 liter
pH	9.8

For use as a surface developer (M-AA-2), 0.5 gram of α -picolinium- β -phenylethyl bromide was added per liter as accelerator to M-AA-1. This compound was dis-

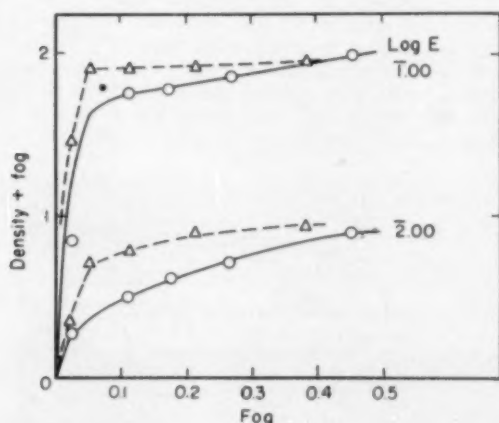


Fig. 2. Density versus fog curves for development of motion-picture negative film in: —○—○—, D-19; —△—△—, M-AA-2.

solved separately in a small amount of water and added before the volume of developer was made up to its final value. Figure 1 gives a comparison of the performance of this developer (M-AA-2) with the glycine surface developer⁴ and with Kodak D-19 for development of a motion-picture positive emulsion to equal fog values (0.05-0.06). The shape of the curve obtained with M-AA-2 is almost identical with that developed by D-19, and the difference in speed is slight. When development was carried to higher fog values, the two curves coincided. On the other hand, the M-AA-2 curve shows substantially higher gamma and speed values than the glycine developer. Strips of exposed film which were subsequently bleached in a 0.3 percent potassium ferricyanide solution containing 3 milligrams of phenosafranin per liter showed not even a trace of an image when developed up to 60 minutes in the M-AA-2 developer, whereas a definite image appeared in D-19 in less than 6 minutes (Curve 4, Fig. 1).

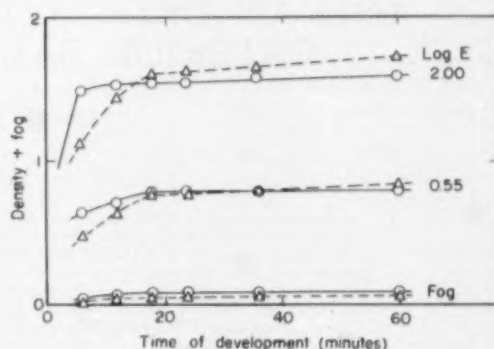


Fig. 3. Development of internal latent image in motion-picture positive film by: —○—○—, D-19 plus 10 grams hypo; —△—△—, M-AA-1 plus 3 grams hypo.

Excessive fog was encountered when this developer was used with motion-picture negative film, but the fog showed the characteristics of aerial fog, and the addition of 5 cc. of 0.1 percent phenosafranin solution per liter of M-AA-2 developer suppressed it. The copper-sequestering agent, 8-hydroxyquinoline, decreased the fog, but was less effective than the phenosafranin. Figure 2 indicates the results obtained in a comparison of M-AA-2 containing the phenosafranin with D-19 in the development of the negative emulsion. In this figure, image plus fog densities are plotted against fog density for two exposure levels. It is seen that the surface developer actually gives higher image densities for a given fog density than D-19.

The M-AA-1 or M-AA-2 formula can be converted into an internal latent-image developer by the addition of sodium thiosulfate (hypo). Figure 3 shows a comparison of a standard internal developer, D-19 plus 10 grams hypo, with the M-AA-1 developer plus 3 grams hypo for development of motion-picture positive film. In this figure, image density plus fog is plotted against the time of development. The surface image was destroyed prior to development by bathing the film for 5 minutes in the ferricyanide bleach. Although the M-AA solution requires a longer time of development to reach

essentially maximum density, that maximum is somewhat higher than obtained with the D-19 plus hypo solution, and the accompanying fog is somewhat lower. As is true of the D-19-type developer, the amount of hypo required to give optimum results varies with the nature of the emulsion to be developed.

Conclusions

The M-AA-2 developer with the addition of phenosafranin is a satisfactory surface developer for both positive- and negative-type materials. The phenosafranin is unnecessary when the developer is used with the relatively slow positive materials. The developer gives high emulsion speeds and shows no trace of internal

image development. The same developer can be converted to an internal image developer by addition of a few grams of hypo per liter. The presence of the phenosafranin and of α -picolinium- β -phenylethyl bromide is unnecessary for the internal developer. The Metol-*d*-araboascorbic acid developer possesses the distinct advantage for latent-image distribution work that essentially the same developer can be used for both surface and internal latent-image development.

References

1. G. Kornfeld, *J. Optical Soc. Am.*, Vol. 31, p. 598 (1941).
2. W. F. Berg and D. G. Ford, *Phot. J.*, Vol. 89B, p. 31 (1949).
3. Cf. review by W. F. Berg, *Phot. J.*, Vol. 87B, p. 112 (1947).
4. G. W. W. Stevens, *Phot. J.*, Vol. 82, p. 42 (1942).

AN APPLICATION OF MICRO-FLASH PHOTOGRAPHY AND AN OPTICAL LEVER TECHNIQUE TO EXTERIOR BALLISTICS PROBLEMS

Donald R. Beresford*

ABSTRACT

A description is given of the equipment and techniques used in obtaining and recording accurate time-position data during the dynamic cross-wind test firing of a small caliber gun. Experiments conducted at the Naval Ordnance Test Station consisted of firing projectiles from test gun barrels which were mounted at right angles to the direction of motion on fast-moving, rocket-propelled (and retarded), rail-guided carriages. Data required included: position, orientation, and velocity of gun barrel during firing and particularly at time of projectile emergence; muzzle velocity of the projectile; position of impact; and correlated time for all position data. Continuous strip film cameras recorded directly (and in daylight) the position of the carriage and barrel and also the projectile at emergence and in flight. Barrel orientation was determined by a similar camera recording the images of a remotely placed non-repetitive chart in a mirror rigidly mounted on the gun barrel. The optical lever technique was necessary because of dynamic nature of the test and the accuracy required. Photographic illumination was provided and time scales placed on all records by several properly located flash lamps furnishing simultaneous light pulses of one micro-second duration at a 2000 pps rate.

IN THE SOLVING of exterior ballistics problems of gun-fired and rocket-launched projectiles, a wide variety of precise time-position data is required. Because of the dynamic nature of many of the experiments, photographic methods are well suited and sometimes provide the only means for complete and adequate coverage. Even then, special combinations and adaptations of standard equipment and the development of new techniques are necessary.

One such exterior ballistics problem, which is reasonably typical, required an application of microflash photography plus an optical lever technique to secure the data required for a solution. Briefly, the problem concerned the measurement of the effect on the trajectories of small caliber projectiles when they are fired under the condition of relatively high cross-wind. To properly evaluate this cross-wind effect, data were needed on the position, orientation, and velocity of the launching barrel during firing, and particularly at the time of projectile emergence. The position and velocity of the projectile at emergence, during flight, and at

impact were also required. The accuracy of the final answer, i.e., the cross-wind effect depended on having correlated times for all these position data. The solution for cross-wind effect was obtained by comparing the known impact position with that of a predicted impact position which accounted for barrel orientation or aiming point, the velocity and direction of the gun barrel, the velocity and direction of the projectile and the time of flight (for gravity drop calculations).

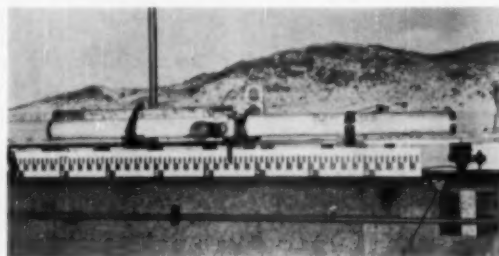


Fig. 1. Gun barrel mounted to fire at right angles to direction of travel on rocket-propelled, rail-guided carriage.

* Naval Ordnance Test Station, Inyokern (Post Office, China Lake), California. Presented at the PSA National Convention in Los Angeles, California, 8 August 1953. Received 28 August 1953.

The first phase of the problem was to arrange to have a projectile fired from a gun barrel under the condition of a high cross-wind in order to have something to measure. This was done by mounting the gun barrel at 90° to the direction of travel on a rocket-propelled rail-guided carriage. See Figure 1. Limitations in length of track and also the supply of gun barrels and carriages dictated, in addition to the booster rockets, a set of retro-rockets to stop the carriage in a recoverable and reusable condition. Electrical contacts and carbon break rods along the rail track provided initiation of the gun firing, the starting of micro-flash lamps, secondary velocity measurements, booster rocket operation, and a rocket-firing safety device. By varying the size and number of booster and retro-rockets, a range of cross-wind velocities from subsonic to well into supersonic values was obtained.

Next a means of recording all the correlated time-position data with the necessary accuracy was required. Primarily this was accomplished with several properly located continuous strip film cameras photographing against special backgrounds the micro-second flash illuminated moving barrel and projectile. The general arrangement of equipment is shown in Figure 2.

The cameras were General Radio oscillograph recorders, through which 100-foot rolls of 35mm Linagraph Ortho safety film were continuously run at approximately 650 inches per second. This meant less than 2 seconds of effective recording time but this was more than adequate to record the required data. A 2-inch focal length lens was used on the cameras for projectile records while a 4-inch focal length lens was used on the carriage position and barrel orientation camera. A lens opening of $f/4$ was normally used with the aperture further masked to give a narrow field of view in the vertical direction, i.e., that in which the film was moving. Normal daylight does not affect film exposed in this manner.

Illumination of the moving barrel and the fired projectile, an effective shutter, and accurate timing for the frames were obtained from pulses of light originating from the Mobile Flash Equipment.¹

Pulses of one micro-second duration light from the General Electric FT-125 flash lamps being operated from this equipment provided energy for both silhouette images of the projectile and direct photographs of the carriage position indicator and the barrel orientation non-repetitive chart. All lamps used were pulsed simultaneously and at an accurately-timed rate of 2,000 pulses per second. With the first flash, i.e., the first frame, being an arbitrary zero, the correlated times for all position data were determined to at least 0.5 milliseconds and with the film moving at a nearly constant speed, interpolation to a much finer precision was possible.

Position and Velocity of the Gun Barrel

One camera equipped with a 4-inch focal length lens was placed 50 feet from the rail track and pointed so that its field of view included the moving carriage for some 12 feet of travel during which space, the gun was electrically-fired by a rail contact and projectile emergence occurred. One flash lamp placed 15 feet from the rail track in line with the camera illuminated the area.

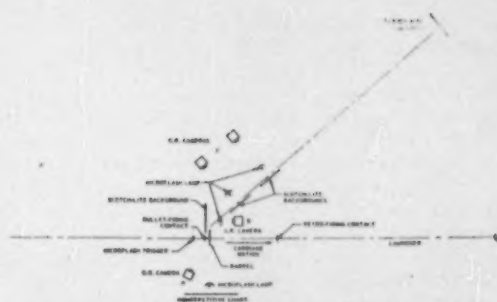


Fig. 2. Arrangement of cameras, lighting and timing equipment and moving carriage for recording the behaviour of projectiles fired from moving barrels.

A pointer attached to the moving carriage appeared against a stationary scale on the track supports. The scale, shown in Figure 1, was graduated in tenths of feet and for high contrast in the photographs had Scotchlite markings. Interpolation of successive frames gave carriage position at time of projectile emergence to within 0.03 feet. The same data were assessed for carriage velocity. The gun firing point was adjusted for the various velocities so that the carriage had a minimum of acceleration at gun firing, i.e., the booster motors were through burning, the retro-motors had not fired and the carriage was "coasting" at nearly a constant velocity. Error analysis indicates gun barrel velocity in the direction of carriage travel was obtained to within 2 feet per second. Secondary velocity measurements over the full length of carriage travel were made by recording signals from magnetic pickup loops on the rail track and also by electronic chronographs whose start and stop signals came from carbon break rods spaced along the rails.

Orientation of the Gun Barrel

The same camera which photographed the moving carriage for position and velocity measurements also photographed a 4-inch diameter front surface mirror which was rigidly attached to the gun barrel and formed part of the optical lever system for obtaining gun barrel orientation. As seen by the camera, the mirror reflected a portion of a non-repetitive chart. The entire

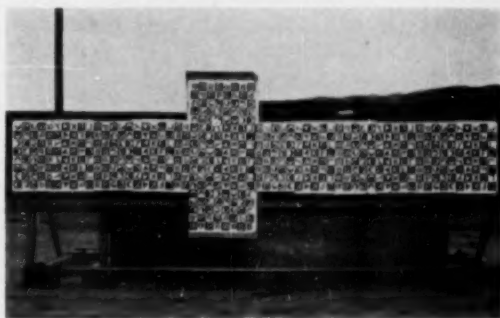


Fig. 3. Chart of non-repetitive characters for recording orientation of gun barrel by means of the optical lever principle.

chart shown in Figure 3 made up of 4-inch by 4-inch individual squares, was 32 inches high and 20 feet long. It was placed 50 feet from and parallel to the rail track. The mirror reflected only portions of this chart for the duration of motion during which the gun was fired and the projectile emerged from the barrel. The use of ten non-symmetrical characters, 4 orientations for each character, photographic reversals, and 2 orientations of 20-inch by 32-inch combinations gave a complete non-repetitive chart as long as at least portions of 2 characters could be seen. Two of the flash lamps illuminated the non-repetitive chart. While the gun was in a stationary position and boresighted to a known point in the target area, a "zero" reading of the non-repetitive chart was made. Using this calibration, the photographs taken during a dynamic test were assessed in conjunction with the barrel position data. With the geometry described above, an angular change in barrel orientation of 1 mil is equivalent to a change in reflected mirror position of 1.2 inches. Error analysis showed that assessment of barrel orientation data was accurate to approximately 0.25 mil. In one series of tests, the "whip" of a long gun barrel was determined and the angular velocity of the barrel taken into account in calculating the theoretical impact point.

Projectile Emergence and Velocity

Another camera was placed so that it viewed the end of the gun barrel at the time of projectile emergence. A single flash lamp placed near the camera illuminated a Scotchlite background and sharp silhouette photographs were obtained of the projectile at emergence and during the first portion of its flight. A second and sometimes a third camera with a similar lamp and background were placed off-range and obtained silhouette photographs of the projectile in flight, 50 and 100 feet from the barrel. A sample of the strip film record is shown in Figure 4. Assessment of the records gave the time of projectile emergence, thus the position of the gun barrel at emergence. Muzzle velocities determined were for practical purposes identical with those obtained by Frankford Arsenal who used the same lot of ammunition and the same test barrels.

Time of Flight and Impact Positions

Because even small variations in carriage velocity and initial projectile velocity would cause considerable shift in actual impact positions, time of flight data was taken electronically. To have a cross-wind effect large enough to measure, the projectile trajectory was arranged to be approximately 1,000 feet. In the impact area the projectile penetrated a double wire screen target giving a stop signal to chronographs whose start signal was correlated to the firing position of the carriage. The impacts themselves were carefully surveyed

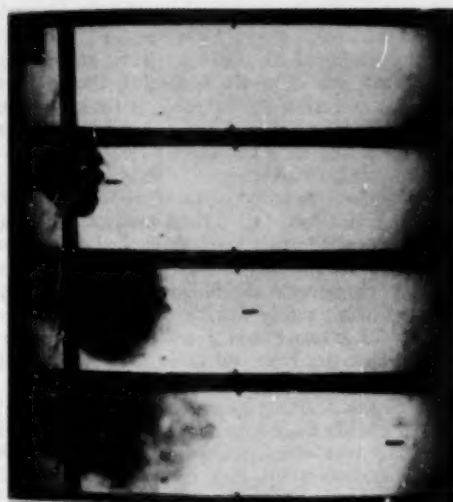


Fig. 4. Projectile emergence records photographed in silhouette by flash lamp against a reflective background.

as to position as were the positions of cameras, carriage position scale, and the non-repetitive chart.

Conclusions

The experiment described in the preceding paragraphs indicates the vital role photography plays in recording accurate data for exterior ballistics problems. Photography supplies the only practical method of obtaining data in a complex experiment. The optical lever technique has proved useful in other tests where data are needed on small mechanical motions which occur as only part of larger dynamic tests. Applications include rocket launcher motion and orientation, and data on other rail-guided devices. The micro-flash silhouette photography technique is a valuable tool for nearly any dynamic exterior ballistic experiment where precise data are required on fast moving bodies. It is used as the primary recording method in the NOTS Aeroballistics Laboratory^{2,3} where accuracies of 0.001 of a foot are obtained on the position of free flight models of rockets, guided missiles, bombs, and other ordnance vehicles including aircraft shapes.

References

1. Ballistics Photography Uses Mobile Flash by E. C. Barkofsky, *Electronics*, June 1952.
2. Barkofsky, Ernest C., "Multiple-Image Silhouette Photography for the NOTS Aeroballistics Laboratory," *Journal of the Society of Motion Picture and Television Engineers*, Vol. 58 (June 1952), pp. 480-486.
3. Barkofsky, E., Hopkins, R., and S. Dorsey, "Microsecond Photography of Rockets in Flight," *Electronics*, Vol. 26 (June 1953), pp. 142-147.